Catalytic Routes to Liquid Aviation Fuels from Lignocellulosic Feedstocks

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Catalytic Routes to Liquid Aviation Fuels from Lignocellulosic Feedstocks

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This thesis is dedicated to my father, Michael J. G. Donnelly, who encouraged and supported me in all that I have done or attempted to do in life. He sadly died just weeks before my PhD was completed.

Abstract

Global warming is perhaps the most urgent and critical problem that we face today. A large proportion of anthropogenic global warming is understood to occur due to the combustion of fossil fuels for the purpose of transportation. The contribution of aviation to global warming has, in recent years become increasingly recognised. Due to the significant increase in passenger air travel predicted in the future we must seek to lessen the impact of aircraft emissions through the development of suitable alternative liquid fuels that may be used within current infrastructure.

Whilst alternative fuels have been developed such biodiesel from triglycerides and bio-ethanol, these utilise food competitive feedstocks, and also exhibit some undesirable physical properties meaning that whilst they may be used in road transport infrastructure, they remain unsuitable for use in aviation. The production of sustainable alternative fuels that possess suitable physical properties for use in aviation, necessitates design of biomass conversion technologies in order that they may yield products which satisfy the stringent criteria set out in aviation turbine fuel standards.

In chapter 2 a biocatalytic route to C10-12 alkane precursors was investigated. A benzaldehyde lyase catalysed conversion of the biomass derived furanic compounds, furfural and 5-hydroxymethylfurfural (5-HMF), was found to carboligate these molecules at room temperature and ambient conditions. The product mixture was found to be tailorable between 10 and 12 carbon chain length precursors.

In chapter 3, the suitability of a low temperature thermochemical conversion technology was explored. A previously reported Pd/C catalysed alkylation was used for alkylation of a theoretical permutation of a product mixture available from Acetone Butanol Ethanol (ABE) fermentation. Whilst straight chain products available through the use of ABE, the substitution of the alcohol constituents for isoamyl alcohol and isobutanol was found to enable production of branched chain aviation fuel precursors, with much improved low temperature properties relative to their straight chain analogues.

In chapter 4 is presented an investigation into a liquid phase pyrolysis technology, with analysis of its efficacy with regard to conversion of a food industry waste to biofuel using zeolite catalysts. Conversion efficiencies were found to be up to 7 %

using the bench scale system in this investigation, however oxygen content of the fuels produced were found to be exceptionally low for a biomass derived feedstock, and as such the process warrants further investigation.

The fuels from chapter 2 and 3 were taken forward for engine testing. Blends of these potential alternative fuels were made up with Jet A-1, and used to power a AMT, mercury HP micro gas turbine. The test cycle used ranged across 4 throttle settings from 0, 30, 60 and 90 %. It was found that whilst emissions for alternative fuel blends remained largely unchanged for most emissions, a difference in thrust was measured, with hydrocarbon fuels providing higher thrust at lower throttle settings and at 60 % and 90 % throttle, oxygenate fuels providing more thrust.

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Dissemination

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Arising primarily from work presented in this thesis:

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Donnelly, J., Muller, C., Wiermans, L., Chuck, C. & Dominguez*, Upgrading biogenic furans: blended C_{10}–C_{12} platform chemicals via lyase-catalyzed carboligations and formation of novel C_{12} –choline chloride-based deep-eutectic-solvents, Green Chemistry, 17, 5, p. 2714-2718.*

Co-authored publications:

Chuck, C. J., Parker, H. J., Jenkins, R. W. & Donnelly, J., *Renewable biofuel additives from the ozonolysis of lignin, Bioresource* Technology **2013,** 143, p. 549-554

Sargeant, L. A., Chuck, C. J., Donnelly, J., Bannister, C. D. & Scott, R. J.*, Optimizing the lipid profile, to produce either a palm oil or biodiesel substitute, by manipulation of the culture conditions for Rhodotorula glutinis,* Biofuels, **2014**, 5, 1, p. 33-43

Conference Contributions

11th International Conference on Renewable Resources and Biorefineries, York, UK, July 2015, Poster presentation, “Catalytic synthesis of a novel transport fuel substitutes from industrially produced fermentation broths”

International Bioenergy Conference, Manchester, UK, March 2014, Poster presentation, “Catalytic synthesis of a novel transport fuel substitutes from industrially produced fermentation broths”

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Abbreviations

Abbreviation	Definition
ABE	Acetone Butanol Ethanol
ASTM	American Standards for Testing and Materials
BAL	Benzaldehyde Lyase
DES	Deep Eutectic Solvents
ECU	Engine Control Unit
EGT	Exhaust Gas Temperature
FAAE	Fatty Acid Alkyl Ester
FAME	Fatty Acid Methyl Ester
FCC	Fluid Catalytic Cracking
FT	Fischer-Tropsch
FT-SPK	Fischer-Tropsch – Synthetic Paraffinic Kerosene
GHG	Greenhouse Gas
HEFA	Hydrotreated Esters and Fatty Acids
HHV	Higher Heating Value
HMF	5-Hydroxymethylfurfural
HT	Hydrotalcite
IAP	Isoamyl Product
IBP	Isobutyl Product
IPCC	International Panel for Climate Change
LCA	Life Cycle Assessment
LH2	Liquid Hydrogen
LHV	Lower Heating Value
LPP	Liquid Phase Pyrolysis

LTO	Landing-Takeoff
MFI	Mordenite Framework Inverted
MGT	Micro Gas Turbine
MTH	Methanol to Hydrocarbon
NMHC	Non Methane Hydrocarbons
NMVOC	Non Methane Volatile Organic Carbons
NOx	Nitrogen Oxides
PM	Particulate Matter
SOx	Sulfur Oxides
SPK	Synthetic Paraffinic Kerosene
THC	Total Hydrocarbons
UAV	Unmanned Aerial Vehicle
USY	Ultra-Stable Y
UTLS	Upper Troposphere – Lower Stratosphere

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Chapter 1

INTRODUCTION

1.1 PROLIFERATION AND CURRENT STATUS OF AIR TRANSPORT

Turbojet engines used for jet engine powered commercial aircraft today were initially invented independently by the British born engineer, Frank Whittle in 1928 and the German engineer, Hans von Ohain, shortly after in 1930.[1, 2] In 1939, the turbojet was used in an aircraft for the first time by the German air force signalling the start of the jet age and the start of the ubiquitous proliferation of the jet engine.[2-4]

The original German engine was designed to be used with gasoline but due to constraints on the supply of gasoline, heating kerosene was used in the case of Frank Whittle's design. Kerosene, now 'Aviation Turbine Fuel' or 'Aviation Kerosene', was widely adopted and the aviation fuel fraction used in today's aircraft is largely similar to this original kerosene fuel.[5]

Aviation kerosene, as a petroleum oil derived fuel has physical properties that are difficult for alternative, renewable liquid fuels to match. Conventional aviation kerosene has higher energy density than many oxygenated alternatives, and its properties well understood owing to many decades of use, meaning that there are no concerns over its compatibility with infrastructure; something which is not clear in the case of many suggested alternatives.[6]

Despite their many positive attributes, reliance on fossil oil derived fuels is undesirable for a number of reasons. Production in geopolitically unstable regions leads to volatility in oil prices and unpredictable operational costs for airlines.[7] Whilst this price volatility was one of the first motivations initiate the search for alternative fuels, in the last 20 years research efforts have been focussed on the search for an alternative due to the environmentally damaging effects of using fossil oil derived aviation fuels.[8]

The inclusion of aviation into the European Union emissions trading scheme in 2012 demonstrates the growing willingness by policy makers to incentivise the development of a more environmentally sustainable aviation industry.[9] The aviation sector has until this point managed to remain largely immune from the negative economic impact of changes to environmental legislation and intergovernmental agreements pertaining to local and global emissions. The slow uptake of more sustainable practices is due in part to the unwillingness of the industry to deviate away from their experience base in conventional fuels, citing safety considerations. It seems that with the advent of better understanding of both fuels technologies and the ever increasingly urgent issue of climate change the aviation industry must invest

more effort into developing sustainable alternatives to a point where their use in air transportation is an everyday reality rather than a research curiosity.

1.1.1 Industry Standard Fuels

The standardisation of fuels in the aviation industry is vitally important for both operational and safety reasons. That a fuel acts in the expected manner when exposed to severe low temperatures is of paramount importance due to the operating environment of aircraft.[10]

The vast majority of aviation turbine fuel used globally falls under one of four internationally recognised and accepted standards from Russia, the UK, the U.S. and China.

Table 1: The four primary aviation fuel standards, used globally

North American Standard	ASTM D1655 for Jet A-1 and Jet A (North America) fuels.
UK Standard	DEF STAN 91-91 for Jet A-1 fuel in the UK
Russian Standard	COST 10227 for TS-1 fuel in Russia
Chinese Standard	GB6537 for No.3 Jet in China

Adherence to specific properties, set out in these standards, ensures compatibility with the global fleet, and avoids cross contamination issues. The most commonly used of these fuels is Jet A-1.[11]

Characteristics of fuel described by the standards are descriptive of a petroleum derived fuel, of which there is historical experience, rather than a list of criteria necessary for successful operation for the required application. Currently it is widely accepted that in order for an alternative fuel to be certificated for use, either as a replacement or blending agent for commercial aviation fuel, it must closely replicate the properties of that fuel. The properties and their mandated minimum and maximum values are set out in each specification and are shown for Jet A-1 in Table 1.1-2.

The molecular makeup of conventional aviation turbine fuel is a complex mix of hydrocarbons with 70-85% straight chain hydrocarbons (Figure 1.1-1). High H:C ratios contribute towards the elevation of gravimetric energy density[12], with aromatics and cyclic compounds reducing this value. The latter do however, impart good low temperature flow properties and seal swelling characteristics necessary for the maintenance and safe continuing operation of aircraft fuels systems.[13] Small quantities of sulfur contribute to undesirable sulfur containing emissions, and much

effort is directed toward production of lower sulfur fuels to mitigate these emissions.[14-17]

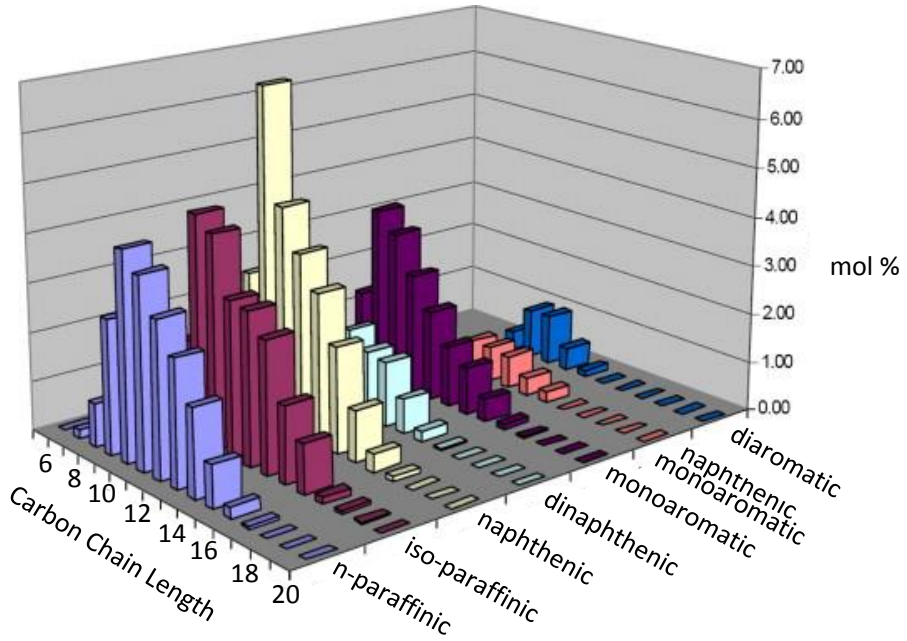


Figure 1.1-1:2D Gas Chromatography analysis of a typical sample of Jet A-1. From Blakey et al. 2011.[13]

Molecular makeup of the fuels will vary depending on the crude oil feedstock and refining parameters used, however fuels will adhere to the relevant standards, and therefore be more or less chemically similar.

Between the certified fuels around the world there are few differences in properties and molecular makeup. Primarily any differences will relate to the cold flow properties of each fuel, with some being designed for use in colder climates and conversely some fuels will be designed for use in warmer climates, allowing a higher freezing point temperature to be permitted. For example, Jet A-1 and No. 3 must have a certified freezing point of less than -47°C and TS-1 a freezing point of less than -50 °C Jet A, typically used in the warmer climate in North America may have a freezing point temperature of up to -40 °C.[18]

The assessment of which criteria require strict adherence for acceptable operation of the aircraft is challenging, though is important when designing alternative aviation fuels. This lack of clear criteria set out by aviation authorities led to a long battle to get the first alternative aviation fuels certified. As more experience is gained using

alternative fuels, it is likely that understanding of what is acceptable will broaden, paving the way for more radical changes later on.

Table 1.1-2: Example of Jet A-1 certificate for compliance with Defence Standard 91-91. This certificate is that of the Jet A-1 used in the research presented within this thesis.

PROPERTY - AV12-00033.001	Units	MIN	MAX	METHOD	RESULT
Appearance	---	--	--	Visual	C+B
Clear, bright & visually free from undissolved water & particles at normal ambient temperature					
Saybolt Colour	---	--	--	ASTM D156	+25
Density at 15°C	kg/m³	775.0	840.0	ASTM D4052	796.1
Density at 15°C - Lower	kg/m³	775.0	840.0	ASTM D4052	796.0
Density at 15°C - Middle	kg/m³	775.0	840.0	ASTM D4052	796.0
Density at 15°C - Upper	kg/m³	775.0	840.0	ASTM D4052	796.0
Density at 15°C - Calculated Mean	kg/m³	775.0	840.0	ASTM D4052	796.0
Abel Flash Point	°C	38.0	--	IP 170	39.0
Existent Gum Content	mg/100ml	--	7	IP 540	1
Freezing Point	°C	--	-47.0	IP 529	-51.0
Initial boiling point (IBP)	°C	--	--	IP 123	146.4
10% Recovered at	°C	--	205.0	IP 123	167.0
20% Recovered at	°C	--	--	IP 123	178.2
50% Recovered at	°C	--	--	IP 123	200.6
90% Recovered at	°C	--	--	IP 123	242.7
Final boiling point (FBP)	°C	--	300.0	IP 123	272.2
% Residue	% (v/v)	--	1.5	IP 123	1.0
% Loss	%	--	1.5	IP 123	0.1
Total Sulphur Content	% (m/m)	--	0.30	ASTM D4294	0.0504
Doctor Test	---	--	--	IP 30	Pos
Mercaptan Sulphur	% (m/m)	--	0.0030	ASTM D3227	0.0004
Kinematic Viscosity at -20°C	cSt	--	8.000	ASTM D445	4.049
Net Heat of Combustion	MJ/kg	42.80	--	ASTM D3338	43.316
Smoke Point	mm	19.0	--	ASTM D1322	25.0
Aromatics, total sample basis	% (v/v)	--	25.0	ASTM D1319	17.1
Copper Strip corrosion (2h / 100°C)	Rating	--	1	IP 154	1
Acid Number	mg KOH/g	--	0.015	ASTM D3242	0.010
MSEP-A (with SDA)	Rating	70	--	ASTM D3948	85
Observed Temperature (Result provided by Client)	°C	--	--	ASTM D2624	12.0 #
Conductivity (U,M,L Average) - Result provided by client	pS/m	50	600	ASTM D2624	298
Heater Tube Control Temperature	°C	260	--	IP 323	260
Heater Tube Deposite Rating	---	--	<3	IP 323	1
<3 Max, no peacock or abnormal tube deposits					
Maximum Pressure Drop	mm Hg	--	25.0	IP 323	<1
Test Time	min	--	--	IP 323	150
Spent Fuel at End of Test	ml	--	--	IP 323	455
Heater Tube Serial No	---	--	--	IP 323	12A03150
Filtration Time	min	--	--	MIL-DTL-83133G (Appendix B)	10
Solids Content	mg/l	--	1.0	MIL-DTL-83133G (Appendix B)	0.2
FAME content of Aviation Fuel by GC-MS					
Total FAME Content	mg/kg	--	5.0	IP 585	<1.8

- Result reported outside published test method limits

1.1.2 Certified Alternative Fuels

The route to certification of an alternative fuel is a long one. The first, a Fisher-Tropsch (FT) fuel developed by Sasol, known as Synthetic Paraffinic Kerosene (SPK) took 10 years from first proposal to approval for use.[19] This is produced via the Fisher-Tropsch process, primarily from coal gas. This semi synthetic aviation fuel was first certified in 1999 through an amendment to the Ministry of Defence standard in the UK.[20] The fully synthetic SPK was certified by a further amendment in 2008.[21] The approval process undertaken by Sasol to allow the use of SPK laid the foundation for the approval of further alternative fuel approval.

There are currently four approved aviation turbine fuel alternatives, which are certified to be blended with conventional aviation turbine fuel in varying proportions.

Table 1.1-3: list of all alternative fuels certified for use as aviation turbine fuel to date.

Fuel	**Acronym**	**Feedstock**	**Approval**	**Year Certified**	**Blending limit**
Fisher Tropsch Synthetic Paraffinic Kerosene	FT-SPK	Coal Gas	Annex A1 ASTM D1655	2009	-
Hydroprocessed Esters & Fatty Acids	HEFA	Animal fats and vegetable oils	Annex A2 ASTM D1655	2011	50 vol%
Synthesised Isoparaffinic Kerosene	SIP	Sugars	Annex A3 ASTM D1655	2014	10 vol%
Alcohol to Jet Synthetic Paraffinic Kerosene	ATJ-SPK	Cellulosic Biomass	Annex A5 ASTM D1655	2016	30 vol%

These fuels have all been shown to operate in an analogous manner to conventional aviation turbine fuels and provide a viable route to alternative fuels for aviation. This potentially addresses one of the concerns that initially incentivised the search for an alternative, that of security of supply.

The environmental impact of these fuels is not necessarily favourable when compared to the use of conventional aviation turbine fuel, this is especially the case where fossil fuels are used as in the case of FT fuels, as the refinement process can be more energy intensive compared with that of conventional crude oil derived fuels.[22] When considering the impact of alternative jet fuels derived from biogenic feedstocks, often one of the main contributory factors in net GHG emissions is the inclusion of land use change effects.[23] When these effects are considered, where a crop is grown on non-marginal land often the GHG impact is often greater for alternative fuels from biogenic feedstocks than the impacts from either conventional jet fuel or those synthetic kerosenes produced from fossil fuel feedstocks.[24]

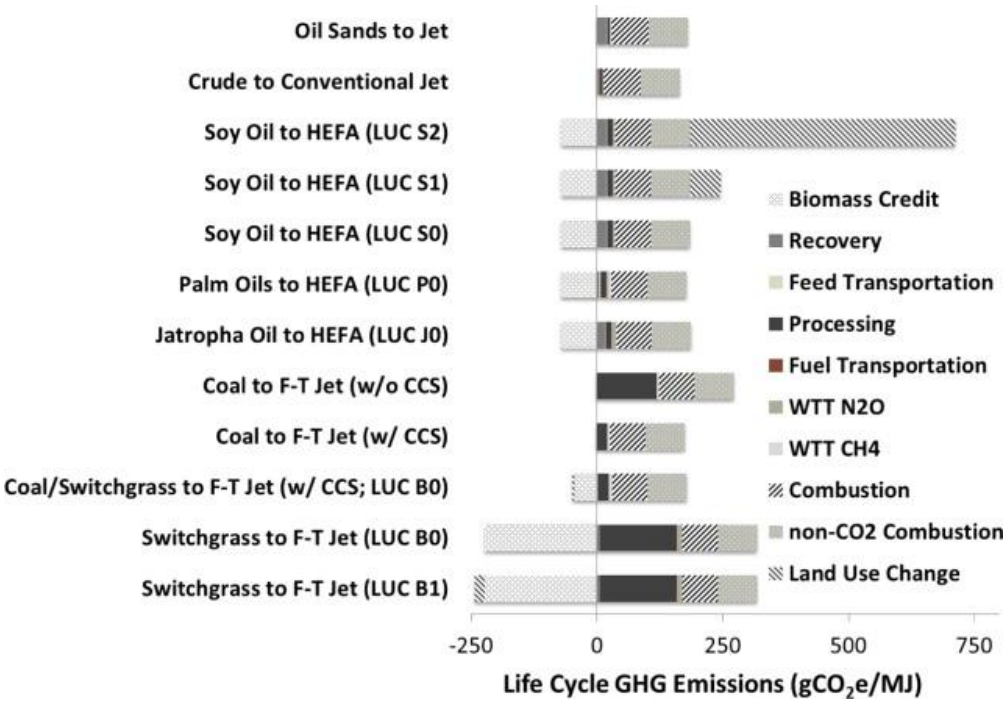


Figure 1.1-2: Results of an LCA study on the GHG emissions of production and use of Conventional and alternative jet fuels. From Hileman et al. [25]

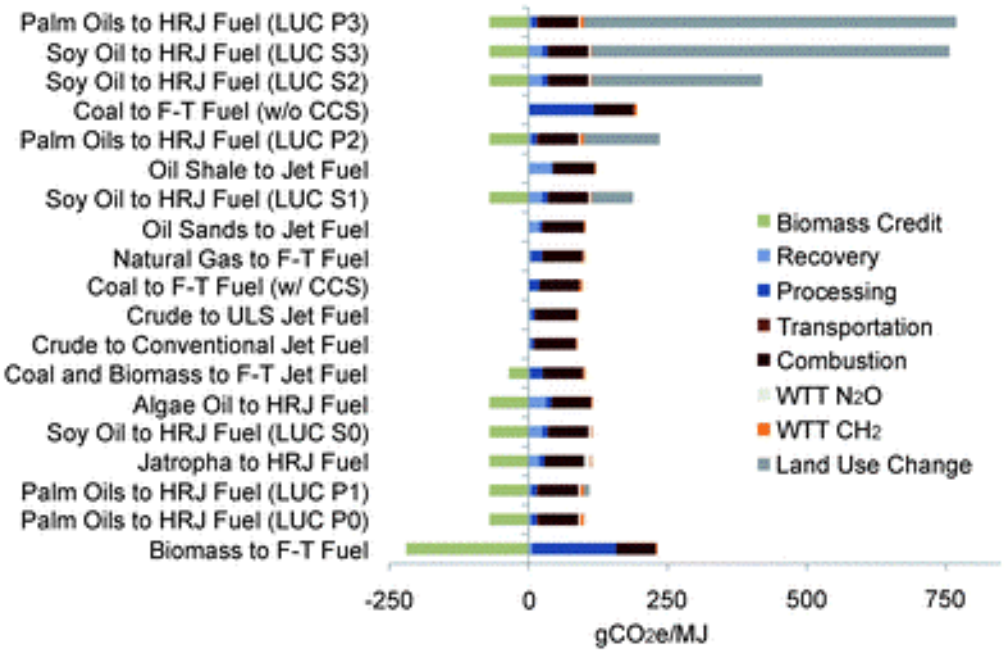


Figure 1.1-3: Results of an LCA study presented by Rye et al.[26]

It is important that any novel fuels produced as sustainable replacements are assessed in such a way that indirect effects are understood, and included in the viability assessment before large scale implementation.

1.2 Other Alternative Technologies

Liquid fuels have been used successfully for over a century and will continue to be used in the short to mid-term at least. However, a range of alternative fuels have also been investigated however, with the intention of fully substituting liquid aviation fuel or to act as a supplementary energy source.

1.2.1 Hydrogen

The fundamental limitation of hydrogen as an energy carrier, is that even in its liquid form (LH_2), its volumetric energy density is around 25% that of kerosene. This would necessitate structural redesign of aircraft in order to maintain the operational capabilities of today's fleet. In addition to this, the tanks would be required to withstand much higher pressures than kerosene tanks, thus increasing their weight.

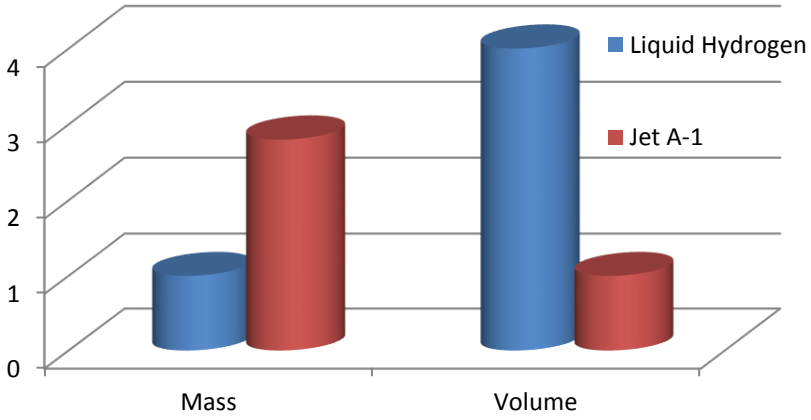


Figure 1.2-1: Relative mass and volume of conventional aviation turbine fuel vs liquid hydrogen. Adapted from Haglind et al.[27]

The majority of emissions from a liquid hydrogen fuel at point of use would be comprised of water vapour and NO_x. Generation of hydrogen would likely incur other lifecycle emissions, not yet quantifiable. The use of hydrogen may be an option for the future of aviation, but in the immediate future it is improbable that it provides a viable solution, from an economic or technical standpoint.

1.2.2 Electric Aircraft

The last decade has witnessed rapid development of battery technology for use in road transportation applications. Battery technology for aviation is severely limited due to the weight of batteries and their associated energy density is not favourable for aviation applications. In the short-midterm, electrically powered aircraft will be limited to experimental aircraft with no useful payload capacity.

There is evidence of interest in battery technology from within the industry, from the perspective of reducing local emissions in the immediate vicinity of airports. This would involve the use of batteries to power the aircraft during the Landing and Take-off (LTO) phases of a flight. This may be used to supplement power from the conventional engines in order to mitigate emissions associated with running turbine engines under high load.[28]

1.3 Environmental Impact of Aviation Fuel Use

In 2015 the global passenger aircraft fleet (≥ 100 seats) was 18 020, with 15 060 freight aircraft (≥ 10 tonnes).[29] These numbers are due to increase by 109 % and 35 % respectively by 2035. More significantly, revenue passenger kilometres (RPK) are expected to increase by 142 %.[30]

In the most comprehensive report of its kind, in 1999 the International Panel for Climate Change (IPCC) reported that aviation emissions are believed to contribute approximately 2% of global CO_2 emissions, and are responsible for approximately 3.5 % of anthropogenic global warming effects once altitude Sensitivities and cirrus cloud enhancement effects are accounted for.[31, 32]

The detrimental effect of each of the components in an aircraft exhaust plume is, to an extent, dependent on the altitude that it is emitted at, leading to altitude sensitivities. Emissions occurring at close to ground level have an increased potential for harmful effects to health in the vicinity of airports, whereas CO_2 emissions are more global in their effects, adding to a global anthropogenic contribution to GHG emissions.[33]

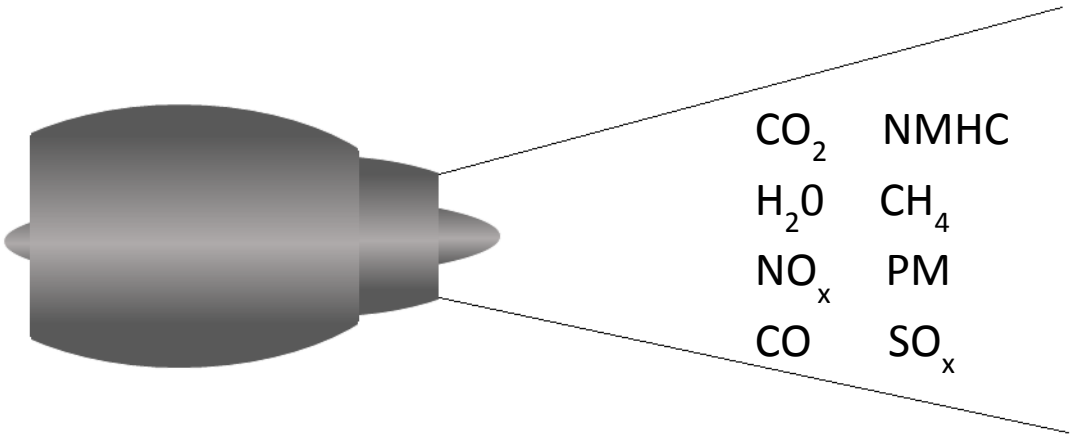


Figure 1.3-1:The main groups of emissions from an aviation gas turbine engine.

The main groups of species found in the exhaust plumes of aviation gas turbines and their potential effects are summarised in Table 1.3-1. The quantities of each category of emission species varies considerably depending on flight phase and flight duration. This is something which should factor into discussion about alternative aviation fuels,

and perhaps gives rise to the suggestion that certain flights should use higher proportions of potentially less polluting fuels.

Table 1.3-1: Gas turbine emissions burning conventional fuels.

Major Species	**Typical Concentration (% Volume)**	**Source**
Nitrogen (N_2)	66 - 72	Inlet Air
Oxygen (O_2)	12 - 18	Inlet Air
Carbon Dioxide (CO_2)	1 - 5	Oxidation of Fuel Carbon
Water Vapor (H_2O)	1 - 5	Oxidation of Fuel Hydrogen
Minor Species Pollutants	**Typical Concentration (PPMV)**	**Source**
Nitric Oxide (NO)	20 - 220	Oxidation of Atmosphere Nitrogen
Nitrogen Dioxide (NO_2)	2 - 20	Oxidation of Fuel-Bound Organic Nitrogen
Carbon Monoxide (CO)	5 - 330	Incomplete Oxidation of Fuel Carbon
Sulfur Dioxide (SO_2)	Trace - 100	Oxidation of Fuel-Bound Organic Sulfur
Sulfur Trioxide (SO_3)	Trace - 4	Oxidation of Fuel-Bound Organic Sulfur
Unburned Hydrocarbons (UHC)	5 - 300	Incomplete Oxidation of Fuel or Intermediates
Particulate Matter Smoke	Trace - 25	Inlet Ingestion, Fuel Ash, Hot-Gas-Path Attrition, Incomplete Oxidation of Fuel or Intermediates

1.3.1 Particulate matter (PM) Emissions

Particulate matter is formed during combustion of aviation kerosene and also in the immediate vicinity of the exit of the engine in the high temperature environment constituting the majority of any aerosol present.[34] Whilst the exact impact of aviation derived aerosols is debated in the literature and in industry, the delivery of PM into the upper troposphere is generally accepted to provide points of nucleation for ice particles in existing clouds as well as acting as a nucleation point for water from the jet exhaust leading to the formation of 'aviation induced cirrus cloudiness', where clouds are formed where there were none previously. PM also serves as a condensation point for more volatile exhaust components in the wider exhaust plume, providing a surface that allows for heterogeneously catalysed chemistry to occur, most significantly leading to the expedition of O_3 formation. This is known to have deleterious effects on the health of both people and wildlife in the vicinity of airports.

1.3.2 CO_2 emissions

The effect of CO_2 emissions are well documented in the academic literature as well as reports by intergovernmental bodies.[35-41] Increasing CO_2 is widely accepted to be a key factor in increasing global warming. The emission of CO_2 does not have the

same localised effects as other emissions, however the reduction of its emission poses the most pressing and challenging task. As the primary product formed during combustion of aviation kerosene, the quantities of CO_2 dwarf those of other emissions, with slight variations in emissions ratios being seen depending on the duration of flights (Table 1.3-2). On average, for each kg of aviation fuel burned, approximately 3.15 kg of CO_2 is released into the atmosphere.[8] The quantity of CO_2 released through combustion of biomass derived fuels is comparable at point of use, however during biomass growth this carbon is sequestered from the atmosphere, thus giving a reduced net CO_2 emission relative to fossil fuels. The reduction of CO_2 is paramount in the search for alternative, sustainable aviation fuels, and this is the driver for much of the research in this field.

1.3.3 NO_x Emissions

NO_x is an abbreviation which refers to total emissions of nitrogen oxides. It is the third most abundant emission from aircraft engines, with 5-25 g being emitted per kg of jet fuel burned.[31] The emission of NO_x at ground level, can catalyse the formation of O_3, which has been shown to be detrimental to human health. As such the minimization of NO_x production, is of high relevance from a legislative point of view, with local air quality issues often cited in disputes over airport expansion.[42]

It has been estimated that the increase of NO_x concentrations in the upper troposphere due to subsonic aviation has been in the order of 20-35 %.[43] The atmospheric impact of NO_x is a very complex one, with its specific impact being reliant not only on concentration, but also the altitudes and atmospheric conditions into which it is emitted. The presence of hydrocarbon derived radicals and -OH radicals both have a profound effect on concentrations, due to alterations in the balance and establishment of radical cycling equilibria. NO_x catalyses the formation of ozone at certain concentrations, but at high or very low concentrations also catalyses ozone destruction.

When considering the global warming potential of NO_x emissions, one must also consider the ability of O_3 to react with and destroy methane, a potent GHG with a lifetime in the upper troposphere- lower stratosphere (UTLS) of approximately 100 years.[44]

Overall, the emission of NO_x into the atmosphere has a varying and uncertain effect on global warming due to the destruction of methane, but also the effect of ozone

itself as a GHG. What is more certain, is that from a local air quality perspective, high emissions of NO_x is undesirable due to concerns over its effect on health.[45]

1.3.4 H_2O Emissions

For each kg of fuel burned in an aircraft engine, 1.26 kg of H_2O is released to the atmosphere.[8] The global warming potential of water vapour is highly uncertain, however values reported are in the range 0.1-0.23 compared with the GWP of CO_2 of 1.00.[46]

1.3.5 CO Emissions

CO is a weak GHG, however it plays a role in global warming concerns in that it reacts readily with radicals within the exhaust plume, mitigating the formation of ozone. CO in itself is however, harmful to human health and is therefore an undesirable pollutant from a local air quality perspective.[47] The presence of elevated levels of carbon monoxide is indicative of a poor quality combustion, potentially caused by poor fuel properties or unsuitable engine conditions. CO is generally formed in the absence of enough oxygen to complete combustion, and so may indicate a fuel rich mixture or inadequate vaporisation and mixing due to high viscosities and poor atomisation.[48]

1.3.6 Non-Methane Hydrocarbon (NMHC) Emissions

NMHCs are produced as a result of incomplete combustion of fuel. They are generally small molecules, with the majority of NMHC emissions being made up of ethene, acetylene, formaldehyde and some aromatics.[8] NHMCs play a role in the catalytic production of O_3 in the UTLS and are thus part of the larger system of emissions interactions that contributes to the overall positive warming effect of aviation emissions upon the atmosphere.

Table 1.3-2:Averarage emissions intensities for commercial aircraft.[49]

Average fuel use and emissions for Commercial aircraft

Domestic	**Fuel**	**SO_2**	**CO**	**CO_2**	**NO_x**	**NMVOCs**	**CH_4**	**N_2O**
LTO (kg/LTO) - Average fleet	850	0.8	8.1	2680	10.2	2.6	0.3	0.1
LTO (kg/LTO) - Old fleet	1000	1	17	3150	9	3.7	0.4	0.1
Cruise (kg/ton)		1	7	3150	11	0.7	0	0.1
International	**Fuel**	**SO_2**	**CO**	**CO_2**	**NO_x**	**NMVOCs**	**CH_4**	**N_2O**
LTO (kg/LTO) - Average fleet	2500	2.5	50	7900	41	15	1.5	0.2
LTO (kg/LTO) - Old fleet	2400	2.4	101	7560	23.6	66	7	0.2
Cruise (kg/ton)		1	5	3150	17	2.7	0	0.1

Source: IPCC Guidelines on National Greenhouse Gas Inventories. Reference Manual, page 1.98

There is evidently need for a fuel that reduces overall carbon emissions, but also one that with careful engineering could be developed to reduce the alternative emissions that are also so damaging. The capital cost of replacing a single aircraft ranges from £67M to £345M each,[50] with Boeing, a major airframe manufacturer, stating that the average working lifespan of 27.2 years[51]. Therefore the rapid replacement of an entire fleet in order to switch to a radically different fuel system, however attractive, would be virtually impossible. This means that the most likely solution to the problems that the industry faces, will come in the form of a liquid fuel which can be produced from sustainable and readily available feedstocks.

The development of a drop in alternative however is not trivial however. Aviation fuels are required to operate in very demanding conditions, with rapid changes in temperatures of 40 °C or more, down to -20 °C. They must be free flowing at these temperatures and combust in a safe and predictable manner within the aircrafts engines, whilst not forming combustible vapours at temperatures experienced at airports.

1.4 Aviation Gas Turbines

A turbo jet engine is comprised of three main sections, the compressors at the front, the combustion section in the middle, with the turbines at the rear. The ambient air is drawn into the front of the engine by a set of 'low pressure' compressors, and passes through progressively higher-pressure compressors before moving through into the combustion sections of the engine. Into the compressed air is sprayed finely atomised fuel, which in the now hot air, this vaporises rapidly and is ignited. Once ignited, the flame is sustained by continuous injection of air and fuel into the combustion section. Upon combustion, the fuel/air mixture forms combustion products and heat, both causing the expansion of the gaseous mixture. These heated combustion products along with any excess air, are then forced out the rear of the engine, providing thrust. In the process of exiting the engine. A portion of this thrust is harvested by a set of turbines, connected to the compressors by a drive shaft running through the centre of the engine, the turbines driving the continuing compression of air (Figure 1.4-1). Thrust is modulated by adjustment of the quantity of fuel delivered to the engine.

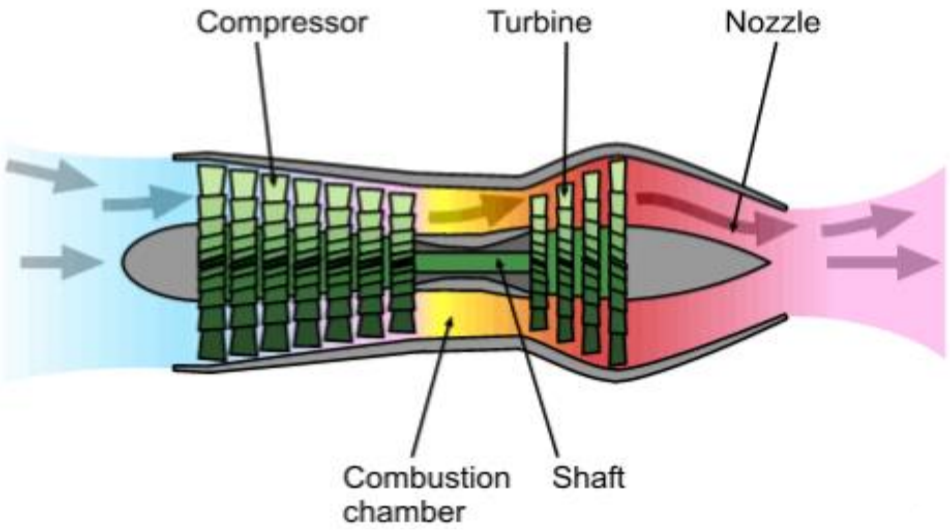


Figure 1.4-1: Schematic drawing of a conventional turbo jet engine.[52]

Modern commercial passenger aircraft use an engine based on the same principle as the turbo jet principle, the turbo fan design (Figure 1.4-2).

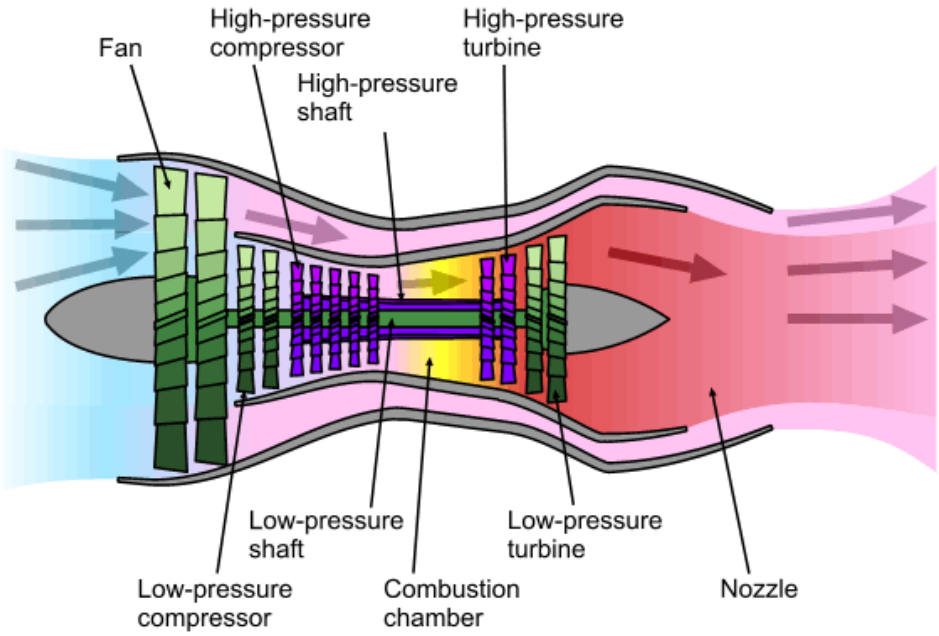


Figure 1.4-2: Schematic drawing of a turbofan engine as used on modern airliners.[52]

Turbo fan engines are more efficient, utilising only a portion of the air inducted into the engine to pass through to the combustion section, with much of it providing thrust but bypassing the compression and combustion sections. This is shown in (Figure 1.4-2) with only the 2 initial compressor stages forcing air through bypass ducts

outside of the combustion section of the engine. This air is then mixed with hot combustion gases at the engine exhaust nozzle.

Gas turbines are not only used in the aviation industry, also being utilised in both large and small scale power generation capacities, as well as power units for marine craft.[53, 54] Much of the research conducted into gas turbines is focussed on static power generation applications. Gas turbines are regularly used in this capacity because the relatively simplistic method of operation of gas turbine engines allows for the use of a whole range of alternative fuels with solid, liquid and gaseous fuels being utilised successfully.[55]

1.5 EMISSIONS TESTING ON GAS TURBINE RIGS

Micro gas turbines (MGTs) operate in the same way as their larger counterparts, usually with less compressor stages and in most cases only one. The vast majority of MGTs used in aviation applications are of the turbo jet rather than the turbo fan design. Commercially, there are two main uses for MGTs; as small scale local power generation units or as engines for unmanned aerial vehicles (UAVs) and large model aircraft.

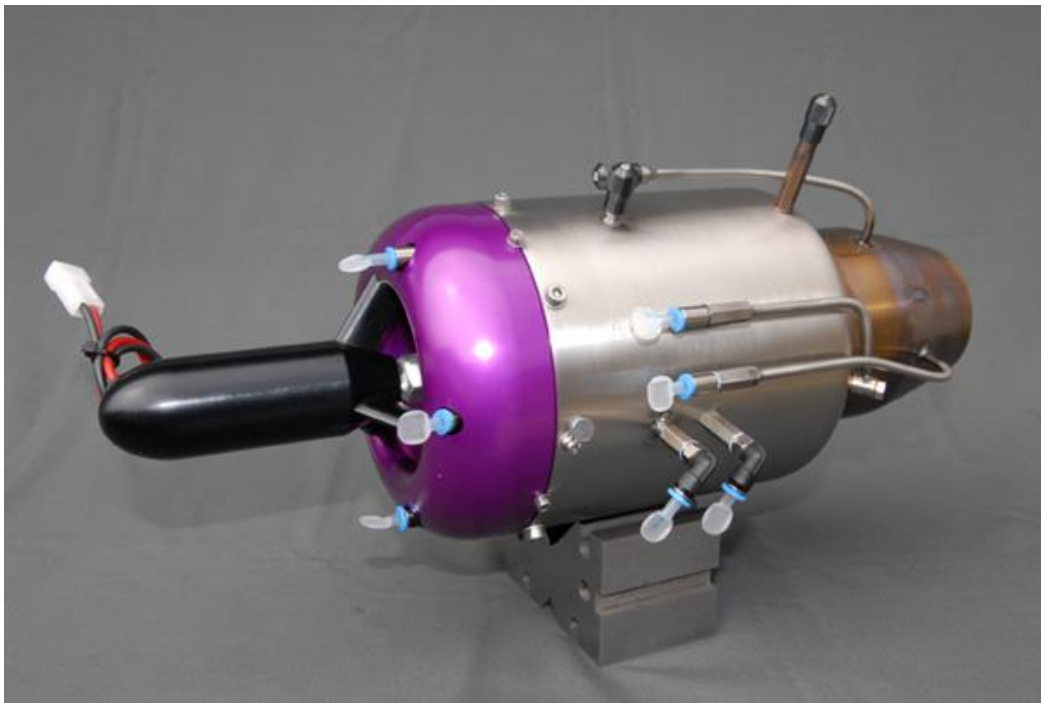


Figure 1.5-1: AMT Olympus micro gas turbine research variant supplied by AMT Netherlands.[56]

Whilst there has been little emissions and performance research for alternative fuels using full scale aviation gas turbines, over the last decade there has been some research focussing on the characteristics of various types of fuels for use in both stationary gas turbines for power generation, micro gas turbines for localised power generation, and a limited number of investigations using micro gas turbines for aviation applications.[55, 57] The use of model aircraft gas turbines adapted for research as shown in Figure 1.5-1 provides a route to low cost, high throughput testing of experimental fuels developed on laboratory scale.

Various fuels have been tested in micro gas turbines. Unrefined vegetable oil and biodiesel also known as Fatty Acid Methyl Esters (FAMEs) are amongst those most tested.[58-62]

The exceptionally high viscosity of vegetable oils can lead to significant differences in combustion characteristics relative to hydrocarbon alternatives. Cavazere et al. found that upon utilizing high blend levels of this lower calorific value fuel with much increased viscosity in a Solar T-62T-32 micro gas turbine, rotational speeds of the engine were reduced relative to when using straight diesel fuel, and injector pressures were increased.[63] For a given fuel mass flow they observed reduced NOx emissions at high vegetable oil blends, with increased CO emissions. Interestingly, blends of 60% oil with 40% diesel fuel produced lower engine speeds, lower NOx and lower exhaust gas temperatures than unblended vegetable oil, however CO values were approximately similar. This would suggest that there was a negative effect on combustion quality caused by the blending of these two potentially incompatible fuels at a high blend level.

Chiaramonti et al. conducted an investigation into the use of vegetable oil in a Garrett GTP 30–67 liquid fuel (diesel) micro gas turbine.[64] Higher CO emissions were observed upon use of vegetable oil. It was found that whilst biodiesel allowed smooth operation of the engine without any pre injection conditioning, the use of vegetable oil required pre-heating to 120 °C to allow for smooth operation, presumably owing to the very high viscosity not allowing for effective injection and vaporisation. It was found that pre-heating and the resulting reduction in viscosity produced reductions in the measured CO emissions to levels similar to those of mineral diesel. This supports the idea that effective atomisation is one of the main contributory factors in good quality combustion and therefore reduction of incomplete combustion products. NO_x emissions were not found to vary significantly between fuels, however the authors noted that differences in values were very close to limits in instrument accuracy.

Chiariello et al. found that the use of vegetable oil in a 30 kW micro gas turbine engine produced comparable quantities of NO_x and CO relative to aviation kerosene at each of four different blend levels.[65] Differences that were observed were within the margin of apparatus sensitivity. It was observed, however, that particulate matter (soot) formation was greatly increased when using vegetable oil blends.

Seljak et al. performed emissions testing using a micro gas turbine using another high viscosity fuel, 'liquified wood' produced through fast pyrolysis processing.[66] It was found again that the use of this very high viscosity fuel led to cold spots in the combustion chamber, leading to inefficient fuel utilisation, and consequently elevated hydrocarbon emissions. The findings of this experiment were confirmed by a later investigation by the same group using similar highly viscous alternative fuels produced through pyrolysis.[67]

Other investigations into the effect of alternative fuels on the operation of gas turbines to an extent, mirror the results of these investigations, most notably where decreases were observed in break specific fuel consumption of an industrial gas turbine utilising biodiesel in place of diesel.[58]

It has been reported that experimental accuracy does not allow for effective differentiation of the emissions data from different fuel blends leading to engine brake power being utilised as a more reliable measure.[64] This difficulty in accurately quantifying emissions from gas turbines arises as a result of the emissions equipment utilised originally being designed for testing of road vehicles, where emissions dilutions are significantly lower and thus the sensitivity of the equipment is not high enough to allow for accurate gas turbine emissions measurements to be made. Until more research has been conducted in this area, it is likely that equipment setups will continue to be sub-optimal and non-standardised. The standardisation of equipment sensitivities, and engine running conditions is necessary for the comparability of results between different investigations. In much the same way as 'drive cycles' are standardised for the efficiency testing of road vehicles, a similar protocol should be implemented for micro gas turbines, for alternative fuels testing.

1.6 FUEL PROPERTIES

The fuel properties of any aviation fuel are crucial to deciding whether they are fit for purpose. An aviation gas turbine engine requires its fuel to be of a consistent and specific physical character in order to ensure reliable, safe and efficient operation. When designing a new alternative aviation fuel, these properties and their effect on the operation of the engine and their impact on emissions must be considered. Some of the individual criteria as specified by the fuel standards are discussed here, along with their likely effect on performance and emissions.

1.6.1 Flash Point Temperature

The flash point temperature of a fuel is primarily of concern from a safety perspective. It is defined as the temperature at which a combustible air/vapour mixture forms above the surface of the bulk fuel, which when exposed to a naked flame will ignite. This criterion is in place to allow for safe handling and storage of aviation fuel. The flash point temperature is affected by the volatility of fuel components. A low flash point fuel is difficult to remediate through blending with a higher flash point fuel, due to the fact that if there remains sufficient volatiles to form a combustible mixture above the fuel mixture, it will fail on this criterion. Effectively, this means that a volatile blend stock could only be added in very low quantities, before breaching this required threshold.

1.6.2 Viscosity

The viscosity of an aviation turbine fuel is one of the most critical physical properties from an operational perspective. The viscosity of jet fuel affects design decisions for the construction of fuels systems, such as pump specifications and fuel line lengths.[68] Viscosity and flow characteristics at low temperature is of particular concern, due to the fact that aircraft operate in temperatures of around -50 °C. Aviation turbine fuel standards specify a particular viscosity at -20 °C to allow for cold temperature operation, significantly higher than the air temperature as the fuel tanks and lines are heated.

1.6.3 Boiling Temperature Profile

The boiling temperature profile of a fuel is descriptive of its volatility. In a conventional jet fuel the boiling temperature of each of the constituents starts at approximately 150 °C and the final boiling component is required to have a boiling point temperature of no more than 300 °C. The varied volatility of the different fuel components have an effect on the evaporation characteristics within the combustion section of the engine with faster evaporation leading to more complete combustion and better fuel efficiencies. The volatility of the fuel is indirectly linked to other properties such as the flash point and the viscosity of the fuel.

When developing alternative aviation turbine fuels, it is common that the potential fuels are unimolecular, or have a very narrow distillation range. This can be problematic as it leads to the formation of fuel rich, air poor regions within the engine, resulting in inefficient combustion and poor fuel economy.[69]

1.6.4 Freezing point

The freezing point temperature and cloud point of a fuel are generally within a couple of degrees of one another. The Jet A-1 specification requires that the fuel has a maximum freezing point temperature of -47 °C. This is a requirement due to the low temperature environments that the fuel is required to operate in. In high latitude and polar flight paths, an even lower freezing fuel such as TS-1 may be used instead. For Jet A-1 the freezing point is determined in the laboratory using the methodology as set out in IP529.[70]

1.6.5 Energy Density & Density

The energy density of the fuel is crucial primarily from an operational perspective. It is also known as the ‘net heat of combustion’ or the ‘higher calorific value’ (HCV), also known as the gross calorific value. The lower calorific value is generally quoted when discussing fuels, although does not generally differ from the HCV significantly. The HCV refers to the amount of energy that is released upon full oxidation of a known quantity of fuel assuming that the latent heat of vaporisation of any water in the fuel is not recovered. The volumetric energy density and the gravimetric energy density are both important parameters in their own right. The gravimetric energy content of the fuel is specified in the fuel standards and is measured using the methodology set out in ASTM D3338. The minimum allowed gravimetric energy density for Jet A-1 is

specified as 42.80 MJ/kg. Whilst the volumetric energy density is not specified in the fuel standards, the density of the fuel is, and therefore, in effect by combination of the gravimetric energy density and density stipulations the volumetric energy density is also regulated.

The HCV of aviation fuel affects the range and payload that is achievable by the aircraft which it is powering. This is as a consequence of the fuel having to produce power enough to propel the aircraft carrying not only the payload, but the weight of the remaining fuel for the journey. This relationship is described by the Breguet equation for range vs payload.[71]

For the majority of commercial passenger transport and commercial freight aircraft, payload is generally the limiting factor, with the maximisation of passengers and freight capacity being the primary objective from an economic standpoint. In long range aircraft and military aircraft, the volumetric capacity of the fuel tanks becomes the limiting factor, and thus the volumetric energy density becomes more of a consideration. Due to this limitation, certain high density fuels have been developed and are utilised by military aircraft in order to maximise their range. These fuels are also often utilised for propulsion of missiles. Two such fuels are JP-10, developed by the US military in the 1970s and later RJ-5. These high density, high energy fuels tend to be comprised of highly sterically stressed molecules such as exo-tetrahydrodicyclopentadiene in the case of JP-10.[72]

1.6.6 Sulfur Content

The sulfur content of a fuel arises due to natural occurrence of the compounds in the crude oil from which the fuel is refined. Concerns over harmful effects of sulfuric emissions, such as sulfur dioxides and mercaptans have led to increased focus on reduction of sulfur content of jet fuels. Jet A-1 sulfur content is determined via the procedure as set out in ASTM D4294. Currently Jet A-1 is limited to 0.3 wt% sulfur containing compounds, and typically contains between 400 and 800 ppm sulfur. This is in contrast with low sulfur ‘euro 5’ road fuels which are limited to 10ppm sulfur content.[73] There is increasing pressure on the aviation industry to address the issue of damage to health due to aviation emissions, and sulfur content of fuels is one of the main focal points, with sulfur dioxide (SO_2) having been linked to illnesses of the upper respiratory system, eye complaints and circulatory and pulmonary issues.[74] Sulfur oxides and sulfuric acid also have a detrimental effect on wildlife and ecosystems in the vicinity of airports and further afield due to the formation of sulfuric

acid in the atmosphere.[75] The process of hydrodesulfurisation used for road transport fuels also reduces the quantities of aromatics within fuels, posing an additional hurdle for aviation fuel, due to the fact that aromatics are considered a necessary species within aviation fuel due to their effect on fuel systems seal swelling characteristics.[76]

1.6.7 Smoke Point

The smoke point of a fuel is the height to which a laminar, well ventilated flame, can grow until incomplete combustion products in the form of smoke, start to emanate from the flame. In general, a higher aromatic content of the fuel will give rise to a lower smoke point and conversely a lower aromatic content gives a higher smoke point. The smoke point of a fuel, or the luminometer number produced, can be quantitatively correlated with the radiant heat output produced by combustion of that particular fuel. This information is used in order to ensure that use of the fuel will not cause excessive thermal stress to the combustor componentry.[77]

1.6.8 Aromatic Content

The aromatic content of Jet A-1 is currently limited to 8 %. There is no combustion related scientific basis for the requirement of aromatics within the fuel, and indeed there is evidence that their inclusion lowers the smoke point and has detrimental effects on the emissions of aircraft. However, it is thought that the presence of aromatics within the fuel acts to plasticise and cause the swelling of seals within the fuels system of aircraft, and thought that the consistent use of non-aromatic containing fuel may cause seal shrinkage and lead to fuel leaks.[78]

1.6.9 Copper Strip Corrosion

Corrosiveness of aviation turbine fuels occurs primarily due to the presence of sulfur species within the fuel remaining from the very high sulfur content of crude oil. If fuel is stored above stagnant water for any length of time, such as in airport fuel tanks, there is the possibility of bacterial growth and the production of corrosive bacterial metabolites within the fuel. In recent years to address this problem antibacterial additives have been added to aviation fuel.

The Copper Strip Corrosion test is used to determine corrosiveness of aviation turbine fuel. The process for this is outlined in D130-12.[79] It involves the submersion of a strip

of copper in a bath of fuel at 100 °C for two hours. The discolouration of the strip is then graded against a standard.

1.6.10 Gum content

The gum content of a fuel is a result of the slow reaction of the less stable hydrocarbon components within the fuel. These are species such as unsaturated hydrocarbons which oxidise, and coagulate into non-liquid 'gums' which can coat fuel system components.[80] This is, for obvious reasons, highly undesirable in the operation of an aircraft. To mitigate this gum formation antioxidants are added to the fuel, however the fuel must meet a certain level of thermal stability in order to be accepted. Gum formation occurs in all gasoline type fuels, however it is of particular importance in aviation due to the increased level of reliability required for safety reasons. Some aircraft, particularly supersonic military aircraft require to use the fuel as a coolant, due to the unavailability of cool air from the aircraft's surface, meaning that the fuel is required to remain stable under unusually high thermal stresses.[81, 82]

1.6.11 Miscibility

Whilst not mandated in fuel specifications, the miscibility of alternative fuels with conventional aviation fuel is a key parameter. Without perfect miscibility, the fuel blend will form a multiple phase mixture in the fuel tanks of the aircraft. It is particularly important to confirm miscibility of oxygenate fuels, due to the difference in polarity between many oxygenates and hydrocarbons within conventional aviation turbine fuel.

1.7 FEEDSTOCKS FOR ALTERNATIVE AVIATION TURBINE FUELS

The development of a sustainable aviation fuel must include consideration of the origins of the feedstock when assessing feasibility. Currently, the vast majority of the biofuels produced globally use food crop feedstocks, with grain and maize being used to produce ethanol along with large proportions of sugar cane in South America. Biodiesel, another first generation biofuel, uses rape seed oil or other triglyceride oils as a feedstock, again, impacting on the market value of these primarily food crops, and displacing food crops in favour of fuel crops.

The production and adoption of first generation biofuels for road transport was incentivised and legislated for by governments across the world, including the European Union.[83] Over the last couple of decades however, the research community and government agencies have increasingly recognised the need for more inclusive life cycle assessments that incorporate as many indirect impacts as possible.[83] Fundamentally the feedstock for fuel should never compete with food production. The use of food for production of fuels is now widely recognised as unsustainable, and many consider it to be unethical.[84]

1.7.1 Lignocellulosic Feedstocks

One alternative is the development of lignocellulosic feedstocks for biofuel production. Lignocellulose is the non-edible portions of biomass and is comprised of polysaccharides, cellulose and hemicellulose with lignin, an aromatic polymer forming a composite structure with the fibres.[85]

1.7.2 Purpose Grown Energy Crops

There are a number of dedicated energy crops that have attracted research focus, generally due to their quick growth, hardiness and ease of processing. A energy crop should also have a low input, both in terms of labour and fertilizers.[86] Grasses fit well with these requirements, leading to the extensive investigation of such grasses as *Miscanthus giganteus*, a perennial C-4 rhizomatous grass from Asia,[87] which has been shown to thrive in cooler climates, as well as warmer ones. This is important for feedstocks in countries in more northern latitudes, as the import of fuel feedstock is undesirable both from economic and environmental perspectives. Another promising feedstock is switchgrass (*Panicum virgatum*) native in more northern latitudes, and initially investigated in north America where it is native.[87] Various other feedstocks are also being investigated for their viability with respect to biofuels production (Table 1.7-1).

Table 1.7-1: Reproduced with permission from 'Biofuels for Aviation'.[88]

Energy Crop	Productivity (Tonne/ha per year)	Suitable Geographic Location
Miscanthus (Miscanthus sp.)	5-43	Temperate
Switchgrass (Panicum virgatum)	5-35	Temperate
Elephant grass (Pennisetum purpureum)	22-31	Temperate, Sub-tropical, Tropical
Canary grass (Phalaris arundinacea)	2-10	Temperate
Giant reed (Arundo donax)	10-30	Temperate, Sub-tropical, Tropical
Energy cane (saccharum sp.)	33-400	Similar to sugarcane
Eucalyptus	10-21	Temperate, Sub-tropical, Tropical
Willow	5-11	Temperate
Poplar	2-34	Temperate
Alfalfa	1-17	Temperate
Sorghum Fibre	16-43	Warm Climates

It is highly likely that the complexion of the feedstock supply chain will be very dependent on climate, logistical and legislative considerations in each individual country around the world, however it would seem that with current advancements in conversion capabilities of cellulosic feedstocks, the proliferation of energy crops will be relatively rapid. Whilst this is positive from the point of view of furthering biofuel adoption and the inevitable associated technological advancements, caution must be exercised and wide ranging life cycle assessments conducted before large scale farming habit changes are permitted or incentivised.

1.7.3 Agricultural Residues

Agricultural residues are a by-product of food production. They are the part of a food crop plant that is generally discarded after or at harvest such as stalks and leaves. It is estimated that between 1.5 – 3.9 billion tonnes of agricultural residues are produced each year.[89, 90] Currently this resource is either left to decompose on the land where

it is grown, or it contributes to the supply of animal feed, or is sold for co-firing in power plant furnaces alongside fossil fuels.[91, 92]

The utilisation of agricultural residues is a promising and relatively underutilised feedstock for liquid fuel production, however it is important to understand all impacts of utilising this resource stream, and consideration must be given to the overall lifecycle impacts of increased animal feed sourcing from other food streams and the impact of increased fertiliser use necessitated by the removal of a large proportion of previously recycled organic material from crop fields.

1.7.4 Food Waste

Approximately 33% of food intended for human consumption is lost in the supply process.[93, 94] It has been estimated that food production currently stands at around 4 billion tonnes per year, with 1.2-2 billion tonnes of this being wasted.[88, 95] The sugar content of food waste is estimated to be between 35.5-69 %,[93] allowing for the possibility of conversion to biofuels through current industrial scale conversion technologies. Whilst food waste would appear to be a logical feedstock from an ethical perspective, logistically, the aggregation of large quantities of widely dispersed food waste is difficult. Urban food waste however, is the large quantities of food wasted in the developed world through such practices as the disposal of foods past their 'sell by' dates. This food is predictable in its composition, and is easier to collect in an economically and logistically viable manner. The available quantity of urban food waste of this type has been estimated at 600m tonnes per year providing a potentially useful quantity of feedstock for production of biofuels.[96] Anaerobic digestion is currently used for the conversion of food wastes to methane which is then burned to generate electricity.

1.7.5 Triglycerides

Triglycerides have for many years provided the feedstock for FAME, known also as biodiesel. Triglycerides for biofuel are generally produced from palm, soya, sunflower, peanut and olive oils.[97] Triglycerides are comprised of a glycerol backbone attached to 3 fatty acid chains. These oils have been proposed for use as straight vegetable oil (SVO) but more commonly they are used for the production of first generation biodiesel through a process of transesterification with short chain alcohols, usually ethanol or methanol (Figure 1.7-1).

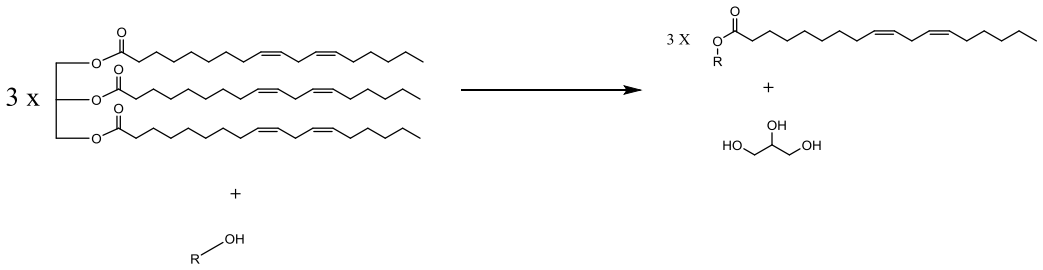
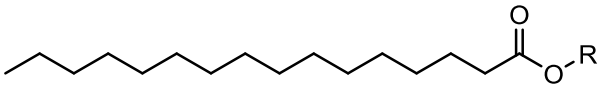
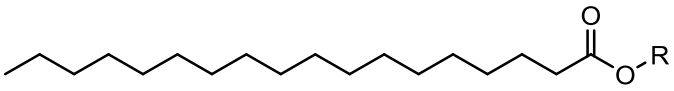
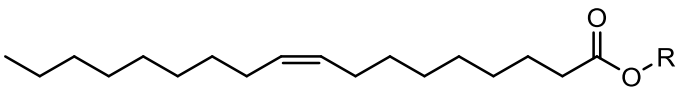
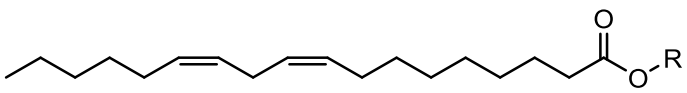
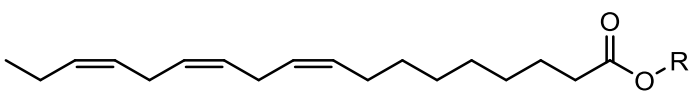


Figure 1.7-1: Transesterification of triglyceride

The majority of FAMEs produced from vegetable oils from these sources fall into one of 5 structural types; palmitic, stearic, oleic, linoleic and linolenic acids (Table 1.7-2: structures of the 5 most common Fatty Acid Alkyl Esters produced from transesterification of vegetable oils). The chemical structure of FAAEs places them at the higher end of the diesel and jet fuels carbon chain length range. Their physical properties differ from those of fossil oil derived fuels, and this has led to speculation as to their suitability for use in existing transport infrastructure.[98] The aviation industry has been particularly sensitive to the potential detrimental effects of biodiesel, banning its presence altogether in the aviation turbine fuel supply chain.

There has also been research focussed on the production of triglycerides from algae, providing a potentially non-food competitive route to biodiesel, and with hydro treatment, bio aviation fuel.[99] The lipid profile from algae tends to be wider than that of non-algal sources, with 16 carbon fatty acids being more prolific.[100]

Table 1.7-2: structures of the 5 most common Fatty Acid Alkyl Esters produced from transesterification of vegetable oils.

Name	Chain	Structure
Palmitic Acid Alkyl Ester	16:0	
Stearic Acid Alkyl Ester	18:0	
Oleic Acid Alkyl Ester	18:1	
Linoleic Acid Alkyl Ester	18:2	
Linolenic Acid Alkyl Ester	18:3	

Currently, triglycerides and other oxygenate products must be deoxygenated prior to being blended with aviation kerosene. The potential of these routes to aviation turbine fuel is explored in the following section.

1.8 HYDRO-PROCESSING FOR AVIATION FUEL

The hydro processing of vegetable oil borrows many of its principles from experience refining and chemical manipulation of crude oil.[101] The application of these techniques to oxygenated fuels from biomass have been further developed and better understood since biodiesel and other oxygenates have started to be considered for aviation.

The approval of Hydroprocessed Esters and Fatty Acids (HEFA) has demonstrated the relevance of triglyceride feedstocks in an aviation context. This hydrogenation step can be carried out in a number of ways using a variety of catalysts.[102] Hydroprocessing of bioderived fuel precursors relies largely on technology developed for hydrocarbon feedstocks, with processing conditions and catalysts optimised to minimise the effect of contaminants commonly found in bio-feedstocks.[103]

1.9 FERMENTATION FOR BIOFUELS

The main method used to convert lignocellulose to date has been fermentation. Fermentation is the conversion of sugars to a range of products such as alcohols, by using a live cell, normally *S. cerevisiae*.[104] Alcoholic fermentation products were being used as a fuel in the early 19th century and in 1826 Samuel Morley had invented an engine which was able to utilise ethanol. In 1908 Henry ford's 'Model T' used ethanol as a fuel, over gasoline.[105, 106] While ethanol has been trialled as a fuel for light low altitude aircraft, the hydroscopic nature, low flash point and low energy density make ethanol unsuitable as a fuel for higher altitude commercial aircraft.

Lignocellulose consists of lignin with a polyphenolic structure, hemicellulose consisting of pentose sugar units, and cellulose comprising of polymerised hexoses. For *S. cerevisiae*, used in conventional ethanol fermentation, only the hexose sugars are able to be readily metabolised. This causes an issue for fermentation for biofuels,

as the majority of the feedstock then, ends up as a low value waste product. The developement of bacterial fermentations have been gathering renewed research interest. [107, 108]

1.9.1 Bio-Ethanol

In recent times, ethanol was initially suggested as a gasoline alternative during the 1970s as a result of the energy crisis. It can be produced via catalytic hydration of ethylene which accounts for approximately 3% of global supply, or more commonly through fermentation processes.[109] Today, bioethanol is by far the most widely adopted and mass produced biofuel produced worldwide. Its incorporation into gasoline has become commonplace in countries around the world. It is able to be blended into gasoline whilst retaining suitability as a fuel for unmodified internal combustion engines in blends of up to 30 %.[110] Production of bioethanol for the fuels industry is currently, largely produced through fermentation of sugar cane. In 2015 world production of bioethanol exceeded 90 billion litres compared with 24 billion litres of biodiesel.[111] Production of bioethanol increased in 2015 by 4.1 % whereas biodiesel production reduced by 4.9 %.[112] Primarily, sugar and starch based feedstocks are used for bioethanol production,[110] with growing interest in lignocellulosic feedstocks as technology for their utilisation become more commercially viable.

1.9.2 Butanol

Butanol has been suggested as a promising alternative renewable fuel, due to its much improved physical properties compared with ethanol.[6] It possesses a higher LCV than ethanol, whilst being less hydrophilic, and more miscible with petroleum fuels. The butanol fermentation was discovered in 1852, and later optimised, eventually resulting in the invention of an industrial application of Acetone Butanol Ethanol (ABE) fermentation, using the bacterium *Clostridium acetobutylicum* in 1912 by Chaim Weizmann, an Academic at Manchester University in England.[105] The process was utilised during the First World War for the production of acetone, needed for cordite manufacture however later development of routes from petrochemical feedstocks proved more economical, and thus ABE fermentation was largely abandoned until more recent interest in sustainable routes to butanol.

It has been reported that butanol can be used in conventional spark ignition engines for road transport in blends of up to 100% with little detrimental effects. In a study conducted into its comparability to Jet A when used in an aviation gas turbine, it was found to have a small reducing effect on thrust, but also observed was a reduction in CO and NO_x. These and other investigations would suggest that the utilisation of biobutanol may indeed be a possibility, and one which offers reduced GHG emissions relative to conventional aviation turbine fuel.

The ABE fermentation produces acetone, butanol and ethanol in a 3:6:1 mass ratio. It is a bacterial fermentation, utilising various strains of the Chlostridum genus; originally and most commonly *Clostridium.acetobutylicum* and later *Clostridium beijerinckii, Clostridium saccharobutylicum and Clostridium saccharoperbutylacetonicum.*[113-115] These bacteria are more generally referred to as solventogenic bacteria.

Whilst lignin cannot be utilised by clostridia, the pentose and hexose sugars resulting from acid hydrolysis pre-treatment can be converted to bio butanol.[116, 117] The main limitation of ABE fermentation for industrial scale fuel production, is that the bacterial metabolites are toxic to the bacteria themselves, thus limiting the concentration of products in the fermentation broth before deactivation of the bacteria.[113] To date, the highest concentration of butanol achieved in a fermentation broth before the deactivation of the bacteria is 3.0 wt.%.[118] Two approaches to solving the problem of product toxicity have been explored in the literature. The continuous removal of solvent from the fermentation broth during fermentation is one approach, and the other is genetic engineering of the bacteria in order to increase resistance to the fermentation products.[119]

Separation techniques include vacuum fermentation, pervaporation, adsorption, gas stripping, pertraction and reverse osmosis.[120-128] It is possible that with the incorporation of these potentially more efficient separation techniques, will allow for ABE fermentation to be a cost competitive route to bio-butanol. Techno economic analysis conducted by Wureshi et al. suggested that the use of membrane technology could serve to reduce the cost of ethanol from ABE fermentation by over 10%, to $0.46 per litre relative to the same process using conventional distillation separation.[129]

1.9.3 Catalytic upgrading of fermentation products

Fermentation products, due to the nature of the mechanisms involved in microbial metabolic pathways tend to produce short chain oxygenated products. Whilst these products have been shown in certain circumstances to be suitable as a drop in fuel in compression ignition and spark ignition engines, due to the more demanding specifications of aviation gas turbine fuels, further upgrading is required. Hydroprocessing of these short chain oxygenates would produce highly volatile C2-C5 products, and therefore is not an option.

In order to increase the energy density of these products such that they may become potential candidates for aviation turbine fuel alternatives, the carbon chain length must be increased to at least C_{10}, and ideally, the C:H ratio lowered by reduction in the number of oxygen containing moieties within the fuel molecules. Whilst the reduction of the amount of oxygen will reduce intermolecular forces to an extent, an increase in chain length will have the opposing effect, and thus a deleterious effect on low temperature fuel properties of the fuel. To mitigate this, the incorporation of branching into the molecules is desirable.

In 2012, Anbarrassan et al. developed a method for the upgrading of ABE fermentation product mixtures to longer chain alcohols and ketones (Figure 1.9-1: Palladium catalysed alkylation of ABE fermentation product mixture[130]).

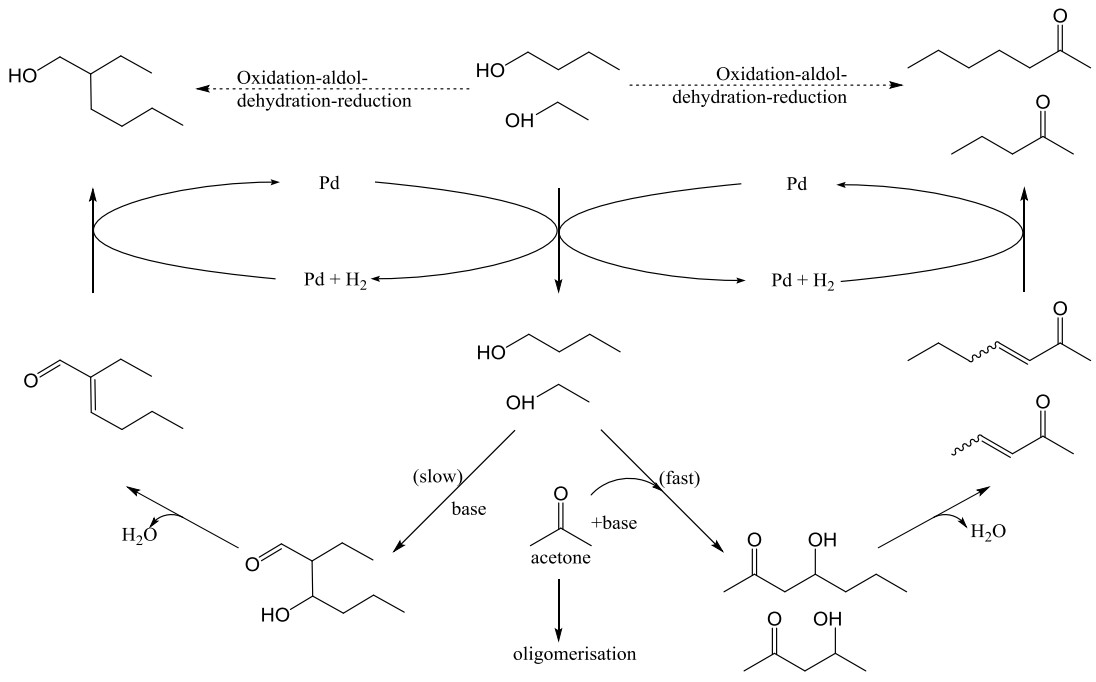


Figure 1.9-1: Palladium catalysed alkylation of ABE fermentation product mixture[130]

The alkylation utilises a ‘hydrogen borrowing’ mechanism, whereby the fermentation alcohols are oxidised to aldehydes, then combine to form an aldol condensate which is dehydrated and further oxidised to form a ‘Guerbet’ alcohol, possessing branching and the 2 position. The predominant mechanism in this particular investigation however, was the combination of the initial aldehyde with the acetone within the ABE product mixture to form longer chain ketones. This method provides the ability to usefully utilise a high proportion of the fermentation product mixture and thus increase the overall efficiency of fuel production through combination of ABE fermentation and a catalytic upgrading step.

Whilst this method provides an ideal route toward alternative diesel fuel components, the product ketone/alcohol mixture has low temperature properties unsuitable for use as a replacement aviation turbine fuel. A conventional, but energy and carbon intense route to deoxygenation is the hydrogenation of the products, however the hydrogenation of alcohols is notoriously energy intensive, and as a renewable alternative fuel, it is highly unlikely that this refinement step would be acceptable from a life cycle analysis point of view. An option for the mitigation of poor low temperature properties is the introduction of branching into the oxygenated molecules. However this would require the use of another alkylation/isomerisation step, or alternatively a fermentation product mixture containing branched molecules.

ABE fermentation product mixtures contain no branched molecules, however there are fermentation processes from the literature which have produced branched molecules.[131-133]

Another option for obtaining branched molecules that can be chemically upgraded using this Pd catalysed route, is the genetic modification of clostridia in order that they can be forced to substitute straight chain alcohol products for branched ones such as isobutanol and isoamyl alcohol. Farnesene, a polyunsaturated isoprenoid is also able to be produced via fermentation utilising genetically modified *S. cerevisiae* yeast through the mevalonate metabolic pathway.[134] This system is perhaps the fermentation derived alternative jet fuel that is closest to commercialisation. The system was developed by the biotechnology company Amyris who in 2016 received further funding from the United States Department of Energy for continuation of their ‘Biofene’ project developing farnesene production for biofuels specifically.[135]

1.9.4 Genetic modification

In order for fermentation technologies, and more specifically ABE fermentation to achieve efficiencies whereby they can be economically competitive with other conversion technologies, it is highly likely that the yeasts and bacteria utilised in the processes will require genetic modification to make it more resistant to product toxicity and also to make it more selective for the desired products. With the rapid advancement of genomics over the last decade, this is becoming possible to do effectively. Primarily, the focus for genetic modification of microbes for fermentation has focussed on increasing their ability to catabolise xylose, the main constituent monomer forming hemicellulose.[136] Whilst broadening the range of biomass constituents able to be utilised has formed the main focus, there has also been research into manipulating the products available through genetic modification. *C. acetobutylicum* has been modified to enhance the production of butanol over other ABE products.[137] It has also been altered to allow for isopropanol rather than acetone production.[138] Other bacteria have been designed to produce branched chain alcohols such as isobutanol and isoamyl alcohol.[139-146]

The advances made in genetic modification, particularly in clostridia, make the possibility of modification of *C. acetobutylicum* to allow the replacement of n-alcohols with branched alcohols, and thus potential for the fermentative production of aviation turbine fuel precursors using already developed catalytic techniques.[130]

1.10 FURANICS AS FUELS

The pre-treatment of lignocellulosic biomass before it is able to be fermented, involves the acid, or enzymatic hydrolysis of the polymeric structures comprising cellulose and hemicellulose. This is to release the pentose and hexose monomers that are able to be metabolised by the microorganisms used in the fermentation process. Beyond fermentation the sugars can be chemically upgraded though dehydration over mineral acids at temperatures of around 400 K to form platform chemicals such as 5-hydroxymethylfurfural (HMF) and furfural.[147-150] Furfural is derived from the pentose sugars obtained from the degradation of hemicellulose, and HMF is derived from the pentose units from the cellulose. Whilst the production of furfural is well understood and relatively optimised, the production of HMF is less so. However it is likely that

over the coming years, the recognition of HMF as a promising platform chemical will incentivise further research and optimisation.

These products can be further upgraded in order to produce commercially and industrially useful chemicals, making them a valuable resource, and thus drawing much interest from the research community.[151-156] Their use as fuels precursors has been suggested by many researchers with interest primarily focussed on the use of furfural but with growing interest in the utilisation of HMF.

However, while they are promising precursors they are extremely toxic to microorganisms.[157, 158] with solutions of 10 mmol/L or lower being inhibitory to most yeast and bacteria. Therefore the conversion of this promising substrate would also require chemical or enzymatic upgrading.

One potential enzymatic route is through the benzaldehyde lyase family of thiamine diphosphate (ThDP)-dependent enzymes. ThDP dependent enzymes are known to have the ability to catalyse a number of chemical C-C bond forming reactions, and are therefore investigated mainly for their application in green synthetic chemistry for fine chemicals and pharmaceutical precursors.[159] Biocatalytic upgrading of readily available chemicals is a potentially attractive route to production of fuel precursors, due to the typically very mild conditions under which the enzymatic catalysis occurs allowing a reduction in the energy intensity of the upgrading process. These advantages apply in existing industry also, with biocatalytic desulfurization of petroleum fuels also being explored in the literature.[160]

Biocatalytic carboligation of furfural and HMF to form alpha hydroxy ketones has been demonstrated in the literature. Whilst at an early stage, the research would suggest that in the future, biocatalytic upgrading could potentially be applied to readily available bioderived platform chemicals and offers a low temperature process with environmentally benign solvents, providing a more sustainable way to upgrade fuels.[161]

1.11 Liquid Phase Pyrolysis

A further method of converting lignocellulose is through pyrolysis. This is one of the most intensively researched conversion routes for lignocellulose to biofuel precursors. Pyrolysis is the process of thermally decomposing the feedstock in the absence of oxygen. It is generally split into two different methods; fast pyrolysis and

slow pyrolysis. Fast pyrolysis has a shorter residence time and is carried out at higher temperatures, whereas slow pyrolysis is carried out at lower temperatures with longer residence times.[162, 163] Longer residence times tend to favour the production of bio-char over the production of a liquid pyrolysis oil or gases (Figure 1.11-1). Residence times for fast pyrolysis processes are typically around one second, whereas for slow pyrolysis residence tends to be over ten minutes, with temperatures of approximately 500 and 300 °C, respectively.[164-166] Fast pyrolysis methods are much more energy efficient than slow pyrolysis, retaining around 60 % of the available biomass energy, as opposed to 33 % in slow pyrolysis.[167]

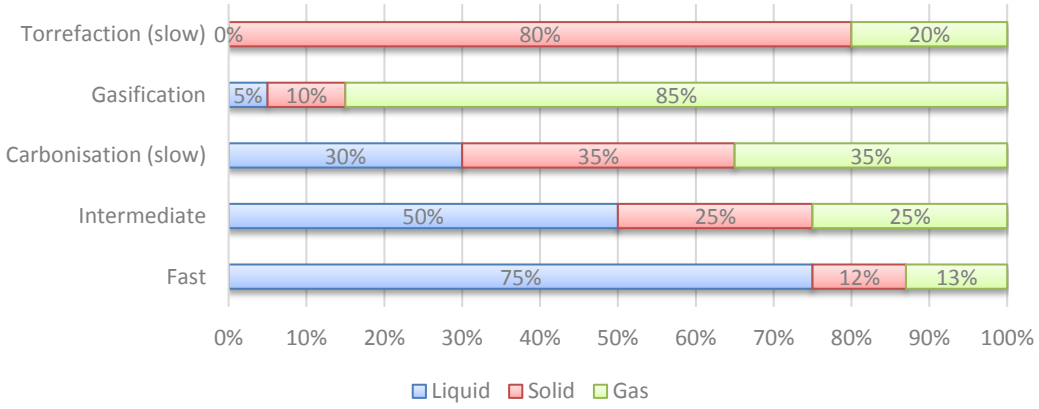


Figure 1.11-1: Typical phase distribution of pyrolysis products. Adapted from Bridgwater et al .[168]

Heat and mass transfer in conventional pyrolysis reactions leads to non-uniform product distributions, and inefficient processing conditions. There have been two solutions to this issue suggested in the literature. One strategy is to utilise fluid bed technology, drawing on experience from many years of fluid bed utilization in the energy generation sector.[169, 170] The other proposed solution is the use of a liquid heat carrier, in which the biomass may be pyrolised. This technique has not attracted a great deal of attention from the research community, but the potential has been recognised by industry and there are a number of efforts to try and optimise this technology.[162, 163]

The liquid carrier tends to be a high boiling (350 °C+) petroleum oil into which the biomass is introduced and dissolved. Wood biomass has been shown to break down at this temperature under ambient pressure conditions to yield a liquid bio oil which remains within the carrier oil. The assertion made by the authors is that the bio oil

may be recovered and used. Interestingly, an increase in liquid biomass derived products was observed with increasing temperature. Of the products obtained (3 % yield) 25% (relative to dry biomass) liquids was obtained at 350 °C, whereas upon increasing the temperature to 390 °C, the proportion of liquid product increases to 34 %.[171] The Alphakat process is sold at pilot plant scale with the claim of being able to transform a wide range of waste and biomass into 'middle distillate' hydrocarbon fuels.[172] These claims are, as yet, uncorroborated by any independent research.

1.12 CONCLUDING REMARKS

The enormity of the challenge of alternative aviation fuel development is one which has led to the advent of a wide breadth of conversion technologies as well as adding to the motivation for the development of efficient and sustainable energy crop production. The state of alternative aviation fuels today is hugely promising, with Sasol having pioneered the certification processes for the first alternative to be approved for commercial use. Subsequent to this approval, in relatively rapid succession, there have been 3 more approvals. Whilst promising, all fuels approved for use must undergo energy intensive and environmentally damaging hydroprocessing.

The new challenge in alternative aviation fuels development is to minimise the negative impacts throughout the production process. This may come in the form of genetic modification of microbes to ferment lignocellulose hydrosylates to saturated hydrocarbons, or perhaps a more benign method of chemical valorisation of biogenic chemicals, such as through biocatalysis or lower temperature thermochemical processes.

Within this investigation, two such methods are investigated, and presented as published papers. The first of these is a palladium catalysed alkylation of a theoretical permutation of the ABE fermentation product mixture, that it was hypothesised could help tailor the properties of the resultant oxygenate fuel for aviation use.[173]

1.13 AIMS & OBJECTIVES

The main aim of this investigation is to investigate potentially promising techniques for the upgrading of biogenic feedstocks to liquid aviation turbine fuels. The intention is that the methods identified and analysed, offer a potentially more sustainable route to an aviation turbine fuel alternative, suitable for use in current turbine technology. The work in this thesis is a presentation of 3 of the conversion techniques investigated, with an analysis of their performance when used to fuel a micro gas turbine.

The three conversion techniques investigated were:

1. Biocatalytic conversion of furanics from biomass hydrosylate into potential 10-12 carbon chain length, aviation fuel pre-cursors.

2. The tailoring of a Pd/C catalysed alkylation for aviation fuel range molecules using a theoretical permutation of a product mixture produced by metabolically engineered bacteria, previously utilised in ABE fermentation.

3. Investigation of a low temperature thermochemical technique, liquid phase pyrolysis, for the conversion of biomass to liquid fuel, through the use of a range of zeolite catalysts.

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Chapter 2

UPGRADING BIOGENIC FURANS: BLENDED C10-C12 PLATFORM CHEMICALS VIA LYASE-CATALYZED CARBOLIGATIONS AND FORMATION OF NOVEL C12 – CHOLINE CHLORIDE-BASED DEEP-EUTECTIC-SOLVENTS

This work was published in Green Chemistry in March 2015. The work was completed in collaboration with the Institut für Technische und Makromolekulare Chemie (ITMC)

Donnelly J., et al., *Upgrading Biogenic Furans: Blended C10-C12 Platform Chemicals via Lyase-Catalyzed Carboligations and Formation of Novel C12 – Choline Chloride-Based Deep-Eutectic-Solvents. Green Chem., 2015,* ***17****, 2714-2718*

2.1 CONTEXT

The production of aviation fuel range molecules through the valorisation of biogenic feedstocks and more specifically, non-food-competitive biogenic feedstocks, is challenging. Hydrolysis of cellulosic biomass yields 5 and 6 carbon chain length monomers, which are able to be utilised by fermentative bacteria and yeasts to upgrade the cellulosic hydrosylate to versatile and valuable platform chemicals.[1]

Production of furanic molecules such as furfural and HMF is well documented in the literature, and due to the versatility of HMF as a potential platform chemical, it has been identified as a chemical likely to be mass produced from biomass feedstocks in the future.[2-6] Investigation into uses of this potentially abundant future feedstock, is therefore of great interest. Depending on the efficiencies of future production techniques of these molecules, their use as aviation fuel precursors may be viable, and therefore, valorisation technologies targeting fuel range species should be investigated now.[2] In any case, new technologies for the manipulation of these molecules can only lead to an increase in their versatility, and as such is of great value to the research community.

Technologies have been developed over the last two decades for production of alternative fuels, and have achieved the goal of producing a technically acceptable and economically viable alternative aviation fuel. Whilst this is an outstanding development, the sustainability credentials of the feedstocks used are often questionable. For example the use of coal gasification in the production of FT-SPK does little to reduce the GWP of aviation emissions as a whole.[8] As well as non-renewables based feedstocks, the conversion technologies themselves are often energy intensive, adding a further environmental cost to their production.

It is necessary to identify and develop conversion technologies, which not only are able to use feedstocks that may be derived from biomass, but also that do not require large amounts of energy. If technologies such as these are able to be developed, it either reduces the overall GWP associated with use of the resultant fuel, or alternatively lessens the pressure to minimise emissions upstream of hydrosylate conversion, making larger scale production of biomass feedstocks more realistic from a logistical and economic standpoint.

In this chapter an enzymatic self and cross-coupling of both furfural and HMF is demonstrated. Benzaldehyde lyase (BAL) has previously been demonstrated to be

capable of coupling a number of aldehydes, however, has not been found to be active with respect to coupling HMF. Here is demonstrated the coupling and cross coupling of furfural and HMF in a room temperature in a largely aqueous media for production of C_{10-12} aviation fuel precursors. Furthermore, an alternative application of these coupled products is demonstrated, with successful utilisation of the carboligated products for production of a novel Deep Eutectic Solvent (DES).

This chapter is submitted in an alternative format in line with Appendix 6A of the 'Specifications for Higher Degree Theses and Portfolios' as required by the University of Bath.

The work completed in the paper presented was conducted by the author with the exception of the following.

Use of the product molecules to for a DES: This was primarily carried out by the paper co-authors, Christoph Müller and Lotte Wiermans.

Genetic engineering of *Pseudomonas fluorescens* and isolation of BAL: This was carried out at RWTH Aachen, by personnel within the Biology department for Dr. Pablo Domiguez de Maria.

2.2 GREEN CHEMISTRY PAPER

UPGRADING BIOGENIC FURANS: BLENDED C10-C12 PLATFORM CHEMICALS VIA LYASE-CATALYZED CARBOLIGATIONS AND FORMATION OF NOVEL C12 – CHOLINE CHLORIDE-BASED DEEP-EUTECTIC-SOLVENTS.**

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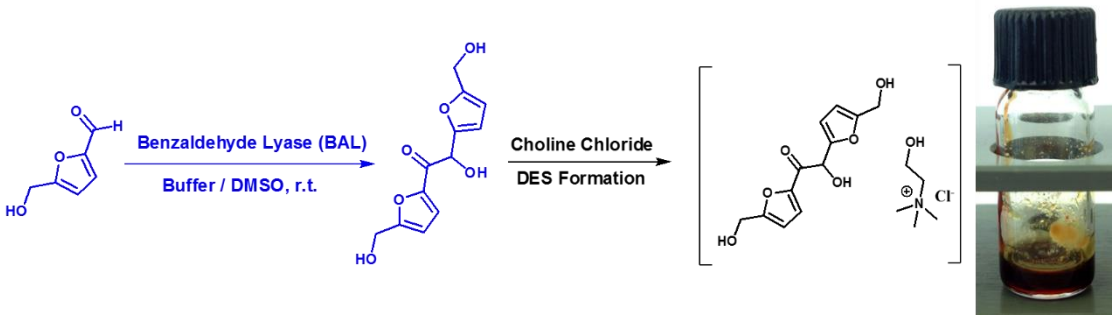
Key-words: Furans; Hydroxymethyl-furfural; Biomass upgrading; Biocatalysis; Lyases; Deep-Eutectic-Solvents

2.3 GRAPHICAL ABSTRACT



Upgrading & Value Generation. Benzaldehyde Lyase (BAL) results an efficient biocatalyst for the *umpolung* carboligation of furfural, HMF, and mixtures of them, leading to blended C_{10}-C_{12} platform chemicals. Subsequently, the mixing and gently heating (< 100 ºC) of the formed hydroxy-ketone with choline chloride leads to the formation of a novel biomass-derived deep-eutectic-solvent.

2.4 SUMMARY

Upgrading 5-hydroxymethyl-furfural (HMF) via *umpolung* carboligation to afford C_{12} platform chemicals may become a useful strategy for biomass valorization. Due to the intrinsic reactivity of HMF, until now only carbene-based organocatalytic approaches have been reported. This communication successfully explores the use of Benzaldehyde Lyase (BAL) for the biocatalytic HMF self-carboligation. Under non-optimized conditions, BAL displays productivities of ~ 7 g hydroxy-ketone L^{-1} h^{-1}, accumulating ~ 35 g L^{-1}. Moreover, mixtures of furfural and HMF lead to cross condensation products, thus providing mixtures with blended C_{10}-C_{12} averages. Finally, the use of the achieved HMF-hydroxy-ketone as hydrogen-bond-donor (HBD) for the formation of choline-chloride-based deep eutectic solvents was successfully evaluated as well, leading to novel series of biomass-derived solvents for the first time.

A key challenge in the production of cellulose-based chemical intermediates, fuels and novel solvents is the cost-effective transformation of highly functionalized carbohydrate moieties into value-added chemicals. One highly promising route is the production of furan derivatives, such as furfural or 5-hydroxymethylfurfural (HMF), from the acid-catalyzed dehydration of hexoses and pentoses. In particular, 5-HMF is extremely versatile and has the potential to become a key precursor to produce a range of chemicals and fuels in a sustainable biorefinery.[1] For example, 5-HMF can be converted into a range of C_4 organic acids suitable for the production of biopolymers by selective oxidation reactions, whereas stable gasoline blending agents (such as dimethyl furan) or solvents (THF) can be produced from decarbonylation and hydrogenation. Moreover, key pharmaceutical precursors can also be produced by amidation or esterification reactions, e.g. the etherification of 5-HMF to yield larger intermediates suitable for retroviral drugs or polymer precursors. However, to further broaden the applications, e.g. to access suitable surfactants or precursors to jet and diesel fuels, the carbon number must be increased to the C_{10}-C_{18} range. This can be achieved chemically through HMF self-condensation – yielding a C_{12} derivative – or from aldol condensation with additional acetone to access higher carbon range precursors.[2-4] Moreover, starting with fractions containing different proportions of furfural and HMF, blended mixtures (C_{10} to C_{12}) may be achieved. All these compounds can then be either partially hydrogenated to retain functionality for additives or fully hydrogenated to yield hydrocarbon fuels.

In this area, a promising but not yet sufficiently explored option for HMF valorization would be its self-condensation in *umpolung* fashion to afford C_{12} platform chemicals, both the formed hydroxy-ketone and the subsequently oxidized diketone. By looking at the highly functionalization of those molecules, from a chemical perspective a broad range of options can be anticipated (Figure 2.4-1).

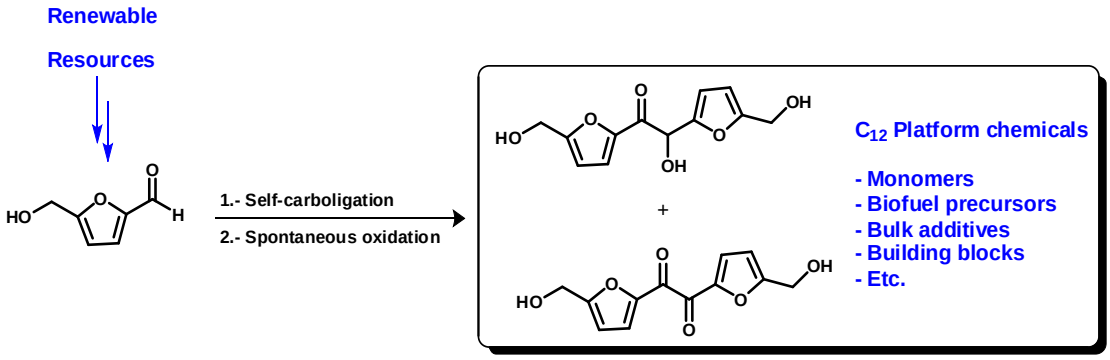


Figure 2.4-1 Self-carboligation of HMF in *umpolung* fashion, produced molecules and some applications thereof.

HMF is highly reactive, being prone to self-oligomerizations, by-product formation and undesired reactions under severe process conditions. Thus, the set-up of HMF-based derivatizations operating under mild and efficient conditions at the same time would become of utmost importance. To this end, for the self-condensation of HMF, organocatalysis – based on NHC carbenes –, has been proposed by several research groups,[5] as a mild technology avoiding product degradation.

In this communication, biocatalysis is successfully assessed for the self-carboligation of HMF for the first time. The use of enzymes and whole-cells has gained considerable interest over the past decades, with an ample range of industrial processes already implemented.[6] Compared to other catalytic technologies, apart from the well-known high selectivities and mild reaction conditions inherent to enzymes, another important asset is that biocatalysts can be produced at large scale *via* fermentation of recombinant microorganisms. Thus, once (bio)catalyst design is performed (e.g. *via* directed evolution), the requested quantities of the enzyme can be straightforwardly produced under environmental conditions. Last but not least,

once the most appropriate biocatalyst has been designed, the use of (immobilized) whole-cells may decrease process costs considerably,[7] an aspect that will become obviously crucial in the production of low-added value (bio)commodities, e.g. the aforementioned HMF-based ones.

For the condensation of HMF the use of lyases,[8] specifically thiamine-diphosphate dependent lyases (ThDP-lyases), was considered. ThDP-Lyases represent a very useful group of enzymes delivering α-hydroxy-ketones along the carboligation of two aldehydes. In this group, Benzaldehyde Lyase (BAL) from *Pseudomonas fluorescens* is a remarkable case, from which many enantio- and diastereo-selective applications including aromatic and aliphatic aldehydes as substrates have been reported over the last years.[8,9] Furthermore, there are some outstanding examples of lyases in general, and BAL in particular, catalyzing highly efficient processes with excellent productivities by means of whole-cell overexpressing systems.[10] Thus, once the proof-of-concept is shown, a subsequent optimization would allow the set-up of a robust biocatalytic process for HMF condensation. The envisaged BAL-catalyzed process is depicted in (Figure 2.4-2).

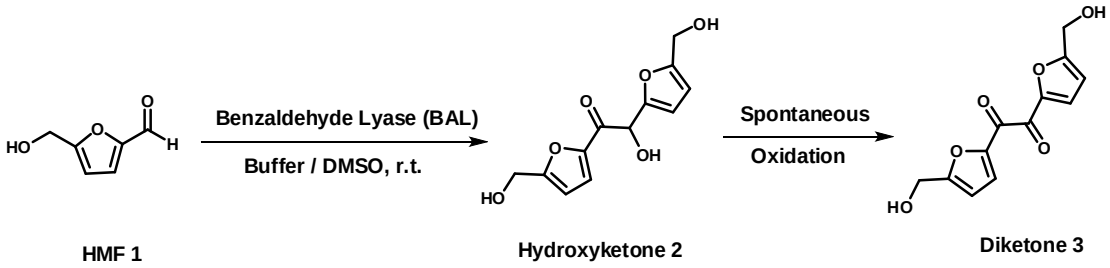


Figure 2.4-2: BAL-catalyzed carboligation of HMF 1 to afford the hydroxy-ketone 2, which may undergo spontaneous oxidation to render the diketone 3.

While BAL-catalyzed furoin production (condensation of furfural to afford C_{10} derivatives) was described years ago,[8,9] to our knowledge the use of lyases for (more challenging) HMF condensation has never been assessed so far. In our concept (Scheme 2), BAL would operate under mild aqueous conditions – using a cosolvent for substrate solubility – at room temperature leading to the formation of the hydroxy-ketone **2**. It may be expected that some spontaneous oxidation of it to afford the diketone **3** may be observed. Kinetic results of the BAL-catalyzed process using HMF (20 mM) for proof-of-principle experiments are depicted in (Figure 2.4-3).

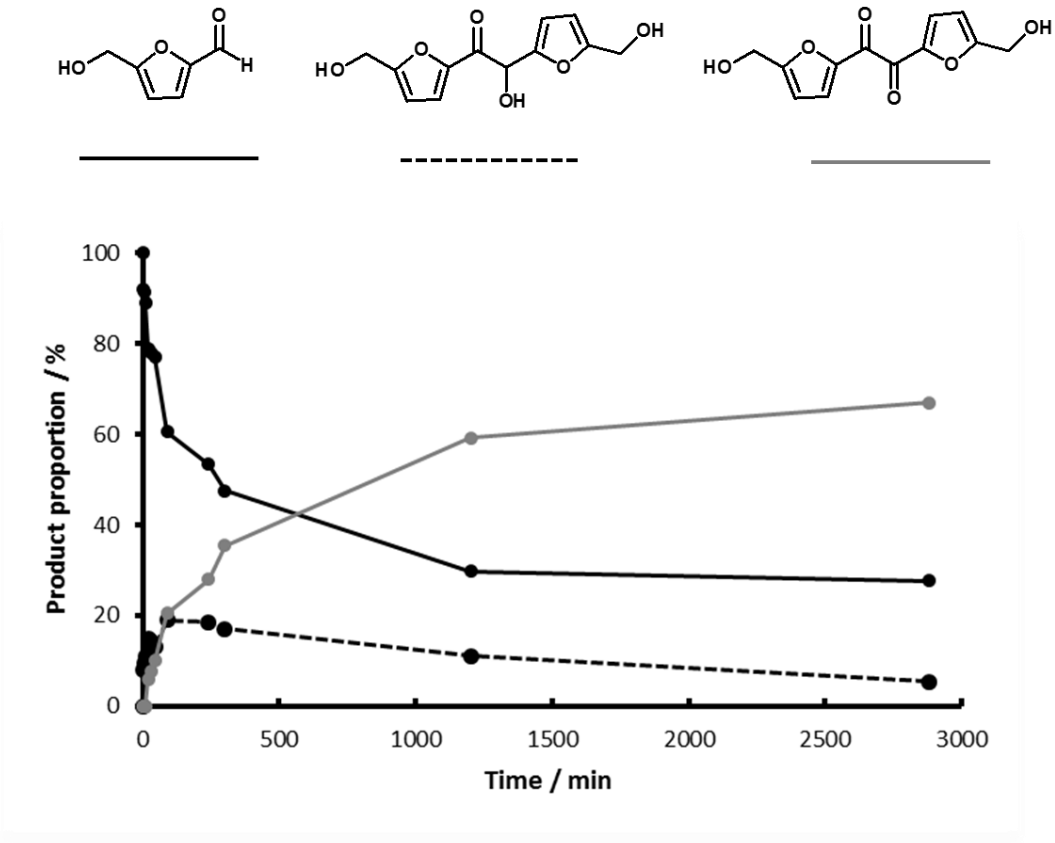


Figure 2.4-3: BAL-catalyzed condensation of HMF. Conditions: 20 mM HMF, 1 mg mL^{-1} BAL, 40 mM ThDP, potassium phosphate buffer (pH 8) with 20 vol% DMSO co-solvent at room temperature.

Gratifyingly, BAL is able to accept HMF as substrate to afford the hydroxy-ketone **1**. Moreover, under these proof-of-concept and non-optimized conditions an initial rate of ~ 7 g L^{-1} h^{-1} of hydroxy-ketone **2** was observed. The reaction proceeded until a conversion of around 70 % was reached. Presumably BAL – herein used as free enzyme (less stable than within a whole cell or immobilized) – becomes deactivated at that time. Furthermore, the oxidized diketone **3** is also observed after some time, formed at the cost of **2**. From a process development viewpoint, the establishment of immobilized BAL-containing whole-cells should enable the stable production of **2** under continuous processing, thus performing rapidly the downstream processing and avoiding further oxidation to the diketone. Nevertheless, it must be noted that both products, **2**, and **3**, may encounter potential applications in many fields.

Once BAL-catalyzed proof-of-concept was successfully shown, further experiments with regard to HMF concentration (20-250 mM) and oxidation patterns were conducted. Reactions were set until 18 h, and then analysed (Figure 2.4-4).

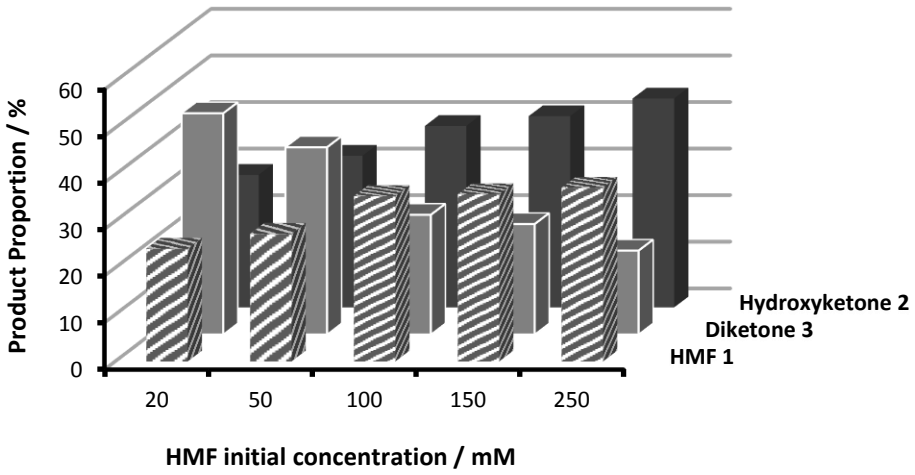


Figure 2.4-4: Ratio of substrate (HMF), hydroxy-ketone and diketone at 18 h and at different HMF concentrations. Conditions: variable 20-250 mM HMF, 1 mg mL^{-1} BAL, 40 mM ThDP, potassium phosphate buffer (pH 8) with 20 vol% DMSO co-solvent at room temperature, 18 h.

Interestingly, BAL is able to perform the carboligation even at higher HMF loadings of up to 250 mM, leading to a remarkable accumulation of ~ 35 g L^{-1} of hydroxy-ketone **2** in 18 h. The presence of the oxidized diketone **3** is detected, yet at significantly lower proportions than in previous experiments (Figure 2.4-4). Presumably, the spontaneous (non-enzymatic) oxidation rate remains constant in all reaction conditions, whereas the enzymatic process undergoes faster at higher concentrations (before the free enzyme gets deactivated), thus accumulating **2** in the reaction system.

Encouraged by these results, subsequently different aqueous mixtures of furfural and HMF were assessed (as they might come from real biorefineries whereby pre-treatment has been conducted). Depending on the initial proportion of both furans, different blended mixtures C_{10}-C_{12} may be expected. This may open a novel way of valorizing such mixtures, especially when mixtures with a Cx average range are needed. Results are depicted in Figure 3.

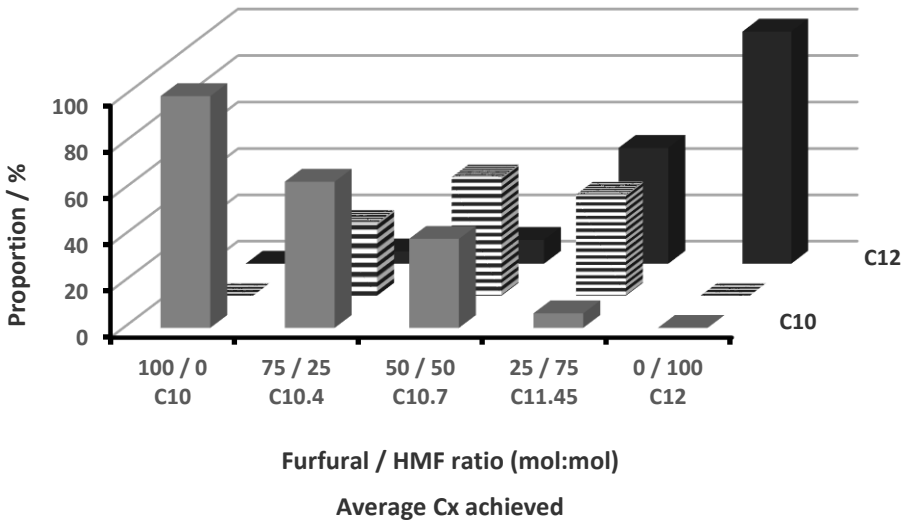


Figure 2.4-5: BAL-catalyzed carboligation of aqueous mixtures of furfural and HMF in different proportions, leading to blended C10-C12 compounds. Conditions: 20 mM total substrate consisting of varying proportions of HMF and furfural, 1 mg mL^{-1} BAL, 40 mM ThDP. potassium phosphate buffer (pH 8) with 20 vol% DMSO co-solvent at room temperature, 18 h.

Gratifyingly, BAL is able to form also mixtures of furfural-HMF, thus leading to C_{11} derivatives. Depending on the initial concentration of the furans, mixtures with Cx averages from C_{10} to C_{12} were achieved. Given the broad substrate range acceptance of BAL (also using aliphatic aldehydes), with the concept herein provided, numerous possibilities for bio-based product upgrading can be envisaged.

Apart from HMF upgrading to C_{12} derivatives, within biorefineries another important trend is the identification of novel biomass-derived neoteric solvents that may be further used for varied applications. For instance, several deep-eutectic-solvents (DES) formed by the combination of a hydrogen-bond donor (HBDs, e.g. alcohols, carboxylic acids) and quaternary ammonium salts, such as choline chloride, have been recently reported.[11] Herein, the obtained HMF-based hydroxy-ketone **2** resulted to be a yellowish solid powder. However, bearing three –OH groups in its structure, it might become a promising HBD to form DES. If successful, this approach might lead to the provision of a series of novel neoteric solvents based on HMF-C_{12} derivatives. Thus, the formation of a deep-eutectic-solvent (DES) between **2** (as model upgrade model) as HBD and choline chloride (1:1 mol: mol) was assessed. Successful results are depicted in Figure 4, where it is seen that the combination and gently mixing (< 100 ºC) of two solids leads to the formation of a stable viscous liquid at room temperature.

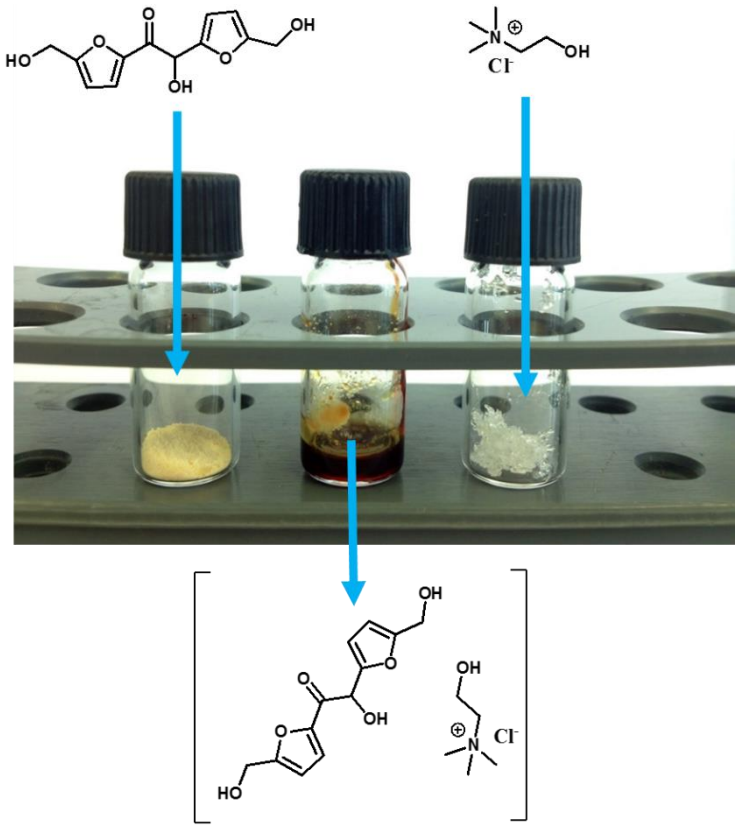


Figure 2.4-6:Formation of a DES composed of hydroxy-ketone 2 (1 mol) and choline chloride (1 mol), to afford a liquid viscous solution at room temperature.

In summary, this communication reports successfully for the first time the use of lyases as biocatalysts for the *umpolung* carboligation to upgrade HMF to C_{12} platform chemicals. Under non-optimized conditions initial rates of ~ 7 g hydroxy-ketone **2** L^{-1} h^{-1} have been observed, with accumulation of the product up to 35 g L^{-1}. Moreover, aqueous mixtures of furfural and HMF can be valorised, leading to blended C_{10}-C_{12} composition, promising for further hydrogenation to deliver tailored blending´s. For these synthetic approaches, the further choice of a better cosolvent – rather than challenging DMSO –, together with biocatalyst design and process set-up (e.g. use of immobilized whole-cells overexpressing BAL) may certainly deliver robust reaction conditions for the valorisation of biogenic furans, furfural and HMF. The inherent intrinsic reactivity of them makes the biocatalytic approach highly appealing for further research and development. Furthermore, the formation of novel DES may lead to novel exciting applications of them as biomaterials and / or solvents.

2.5 EXPERIMENTAL SECTION

Chemicals.- All chemicals were purchased from Sigma-Aldrich and used without further purification. . Benzaldehyde lyase from *Pseudomonas fluorescens* was cloned and overexpressed in *E. coli* cells, and produced by fermentation.[9] After fermentation, BAL was lyophilized and stored at -20°C until use. BAL characterization was performed using benzaldehyde as substrate, and benzoin formation as reaction test, as reported elsewhere.[9]

Standard reaction with BAL for HMF carboligation.- To a mixture of 40 mL potassium phosphate buffer (pH 8) with DMSO (20 vol%) was added ThDP (2 mg, 4.03 x 10^{-3} mmol) and BAL (40 mg). HMF (100.89 mg, 0.8 mmol) was then added to the reaction and the vessel stoppered. The reaction was allowed to stir for 18 h at room temperature. The reaction was quenched by addition of 80 mL EtOAc and the product extracted into the same. EtOAc was removed under reduced pressure and the product dried under high vacuum. Characterisation was effected through NMR spectroscopy.

Standard reaction with BAL with aqueous mixtures of furfural and HMF.- To mixtures of 20 mL potassium phosphate buffer (pH 8) with DMSO (20 vol%) was added ThDP (1mg, 2.02 x 10^{-3} mmol) and BAL (20 mg). HMF and furfural were then added in varying proportions (75/25, 50/50, 25/75) to make up 0.4 mmol total substrate and the reaction vessels stoppered. The reactions were allowed to stir for 18 h at room temperature. The reactions were quenched by addition of 40 mL EtOAc and the products extracted into the same. EtOAc was removed under reduced pressure and the products dried under high vacuum. Characterisation was effected through NMR spectroscopy and mass spectrometry.

DES formation.- 100 mg (0.41 mmol) HMF hydroxyl-ketone **2** and 59.0 mg choline chloride (0.41 mmol) (both solids) were stirred in a GC vial in a molar ratio of 1:1 at 60-70 °C for ~ 1 hour. When cooled down, the viscous liquid remained.

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2.7 SUPPLEMENTARY INFORMATION

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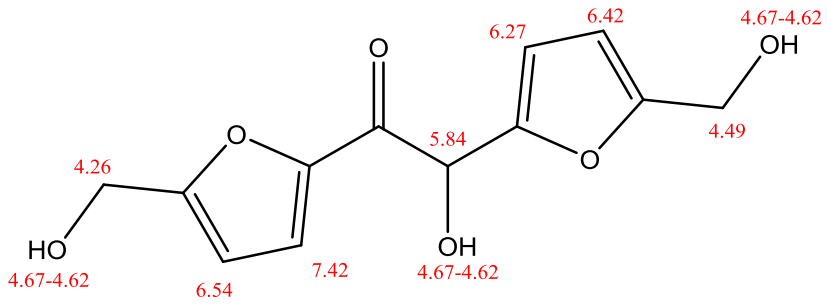
1.- Analytics of products.

NMR-Spectroscopy. NMR spectra for HMF coupled products were recorded on a 300 MHz (^{1} H-NMR: 300 MHz, ^{13}C-NMR: 75 MHz) Bruker device from BioSpin GmbH at 20 °C. ^{1}H NMR spectra for HMF-furfural cross coupled products were recorded on a 500 MHz Bruker Ultrashield Plus device. Chemical shifts are relative to the used solvents (acetone-d_6: ^{1}H: δ = 2.09 ppm, ^{13}C: δ = 30.6 ppm (CD$_3$)), indicated in ppm.

Mass Spectrometry. EI Mass spectra for coupled furfural products were measured with a "Finnigan SSQ 7000" device. Spectra for HMF-furfural coupled products were recorded using a “Bruker MicrOTOF” ESI-TOF device.

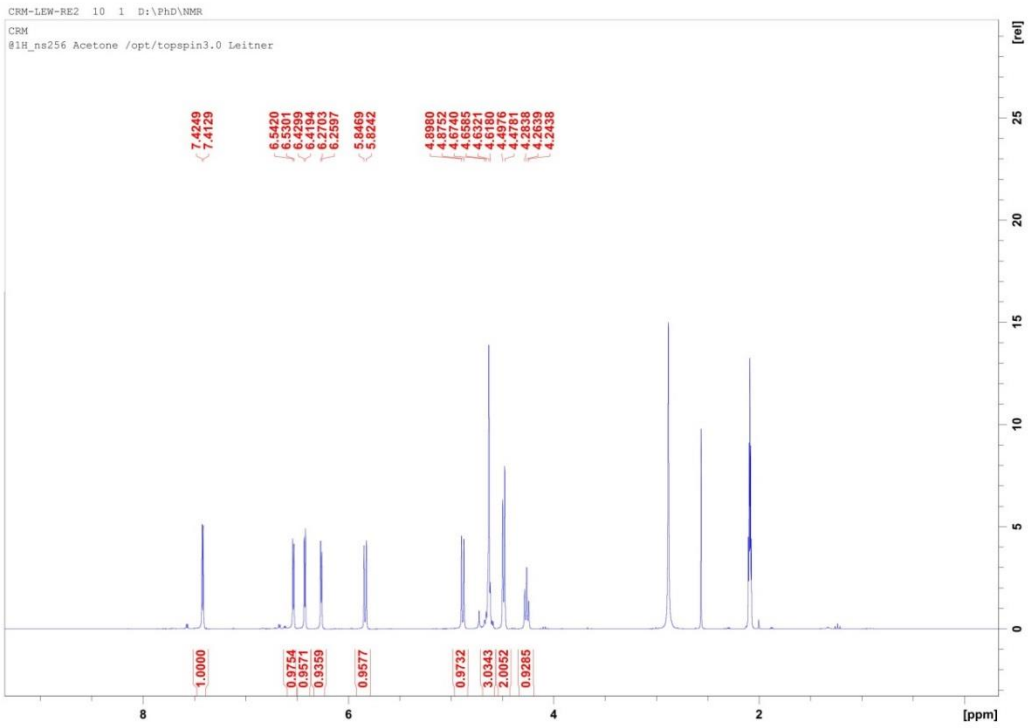
IR Spectroscopy. IR spectra were measured with a "Perkin-Elmer 100FT-IR" spectrometer and detected with an "UATR Diamond/KRS-5" device. The measurement was per-formed as differance spectra versus $CHCl_3$. The unit of the absorption signals is cm^{-1}. Signal intesities are characterized by following abbreviations: vs = very strong (0 - 20 %), s = strong (21 - 40 %), m = medium (41 - 60 %), w = weak (61 - 80 %), vw = very weak (81 - 90 %).

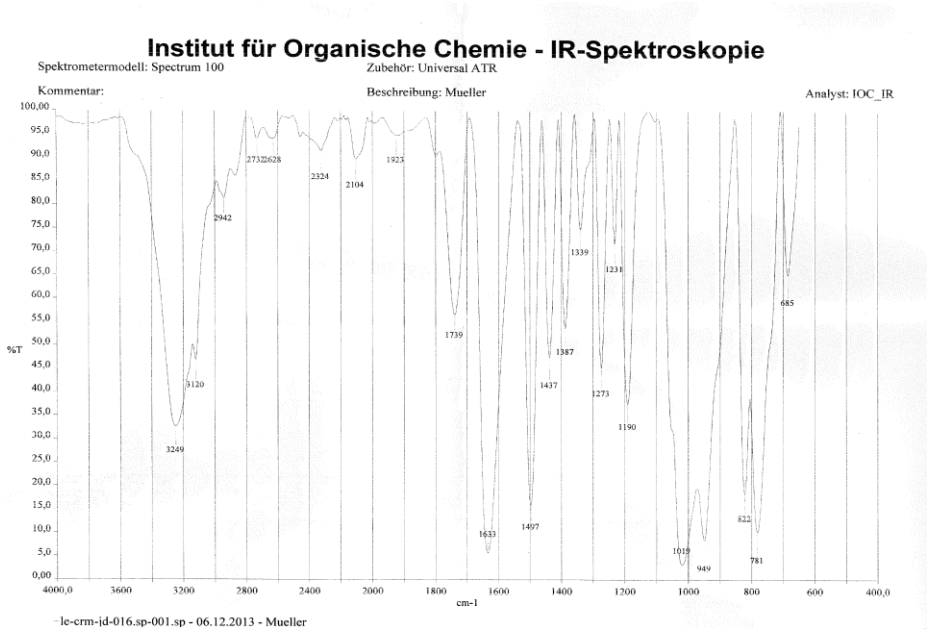
2-hydroxy-1,2-bis(5-(hydroxymethyl)furan-2-yl)ethanone



^{1}H NMR(acetone-d_6): δ 7.42 (d, J = 3.6 Hz, 1 H), 6.54 (d, J = 3.5 Hz, 1 H), 6.42 (d, J = 3.1 Hz, 1 H), 6.27 (d, J = 3.2 Hz, 1 H), 5.84 (d, J = 6.8 Hz, 1 H), 4.67 – 4.62 (m, 3 H), 4.49 (d, J = 5.9 Hz, 1 H), 4.26 (t, J = 6.0 Hz, 1 H) ppm.

^{13}C NMR (acetone-d_6): δ 185.9, 163.1, 157.7, 153.6, 150.7, 122.8, 111.0, 110.8, 109.5, 71.3, 58.3, 58.0 ppm;



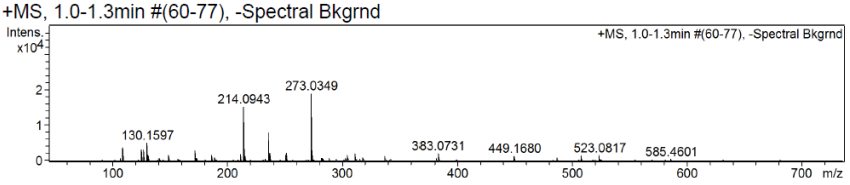


IR: Alcohol stretch of terminal –OH groups (3249 cm^{-1}), Aromatic C=C bend (1633 cm^{-1}), C=O stretch (1739 cm^{-1})

Confirmation of Expected Formula

Sample-ID	ch_jd_dhmf	Submitter	Joseph Donnelly
Analysis Name	ch_jd_dhmf_342088_68_01_46356.d	Supervisor	Chris Chuck
Method used	Confirm Formula Positive 50to500 loop inj.m	Acquisition Date	26/11/2014 10:42:51
Ionisation Mode	positive electrospray (ESI)		

+MS, 1.0-1.3min #(60-77), -Spectral Bkgrnd



#	m/z	I	I %	Area	S/N
1	109.0301	3854	20.3	87	3665.0
2	125.0247	3170	16.7	75	2918.6
3	127.0400	3081	16.2	76	2876.9
4	130.1597	5095	26.8	43	4864.7
5	172.2247	2926	15.4	27	1980.7
6	214.0943	15222	80.1	183	3964.7
7	236.0894	7855	41.3	178	1462.1
8	237.0776	2275	12.0	28	418.0
9	273.0349	18998	100.0	1010	3262.4
10	274.0385	2495	13.1	137	430.8

Generate Molecular Formula Parameters

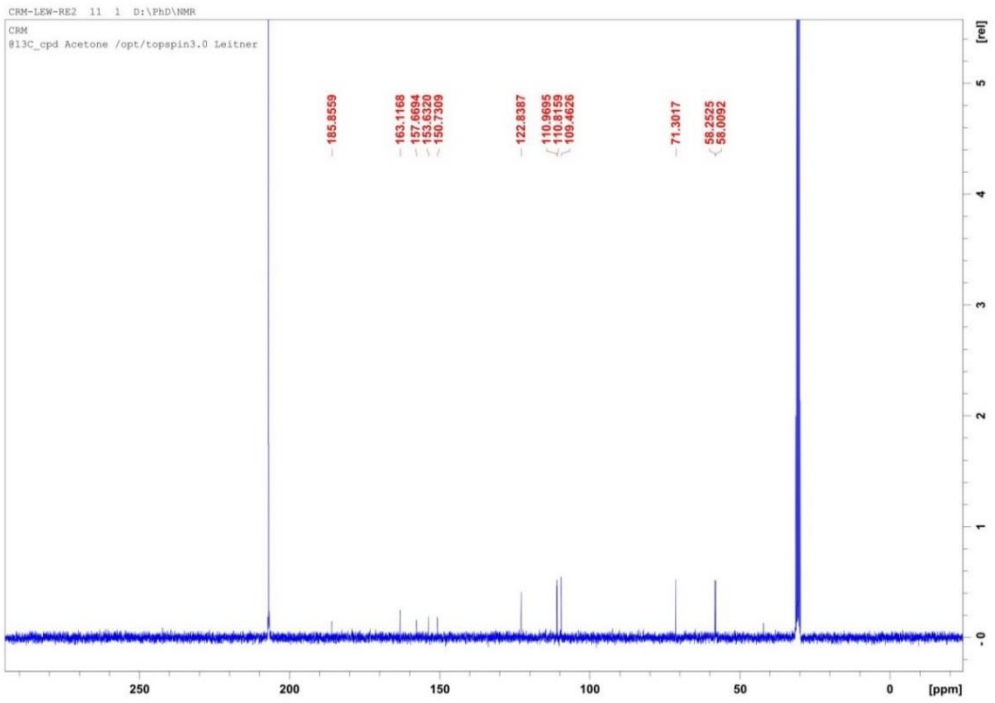
Charge	Tolerance	SearchRadius	H/C Ratio min.	H/C Ratio max.	Electron Conf.	Nitrogen Rule	sigma limit
positive	10 ppm	0.05 m/z	0	3	both	true	0.05

Expected Formula C12 H8 O6 **Adduct(s):** H, Na

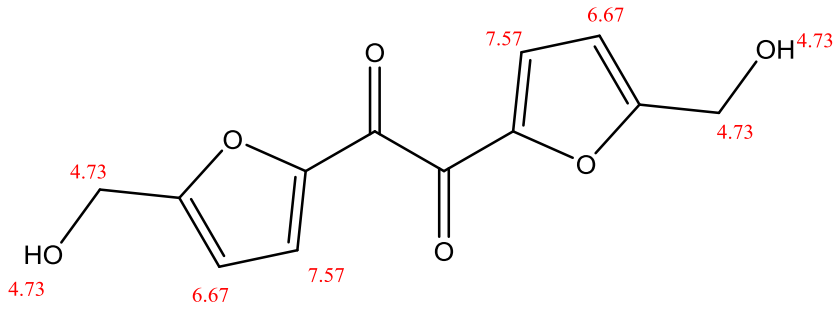
#	meas. m/z	theo. m/z	Err[ppm]	Sigma	Formula

Note: Sigma fits < 0.05 indicates high probability of correct MF, and mass accuracy of 5ppm or better is generally acceptable for publication

MS: 273.0349 corresponds to product + Na^+, Sigma = <0.05



1,2-bis(5-(hydroxymethyl)furan-2-yl)ethane-1,2-dione



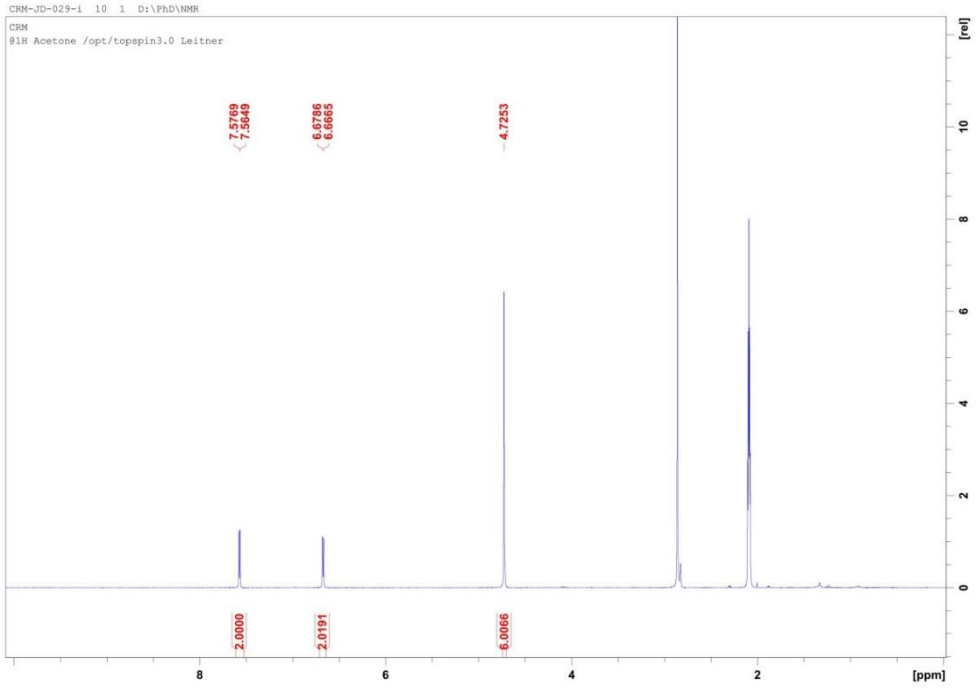
^{1}H NMR(acetone-d_6): δ 7.57 (d, J = 3.6 Hz, 2 H), 6.67 (d, J = 3.6 Hz, 2 H), 4.73 (m, 6 H) ppm;

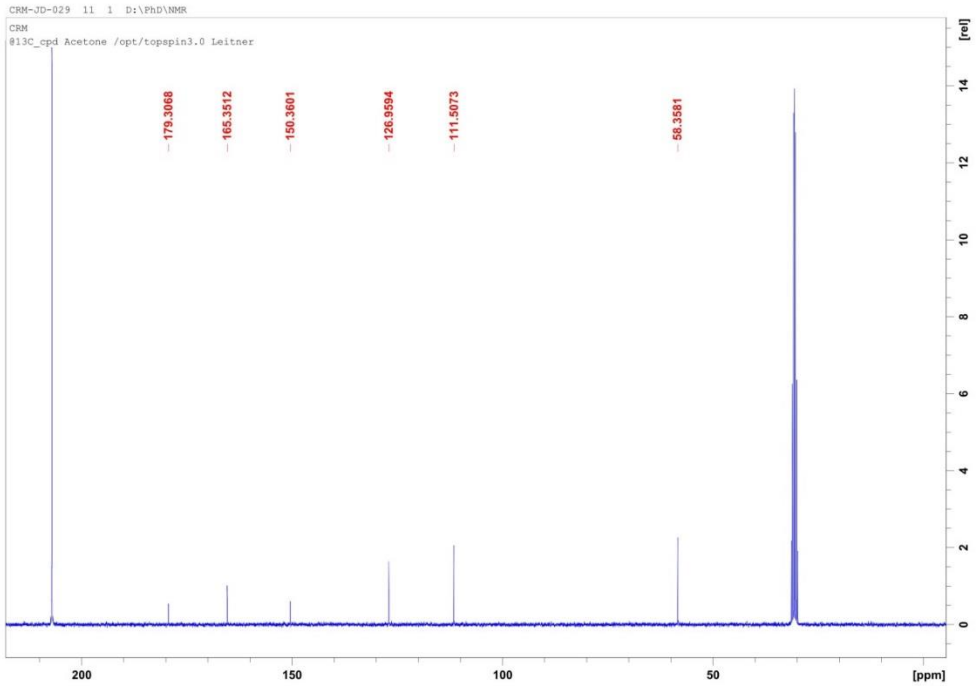
^{13}C NMR (acetone-d_6): δ 179.3, 165.4, 150.4, 127.0, 111.5, 58.4 ppm;

IR (KBr): ν = 3249 (s), 3120 (m), 2942 (vw), 2104 (vw), 1739 (m), 1633 (vs), 1497 (vs), 1437 (m), 1387 (m), 1339 (w), 1273 (m), 1231 (w), 1190 (s), 1019 (vs), 949 (vs), 822 (vs), 781 (vs), 685 (w) cm^{-1};

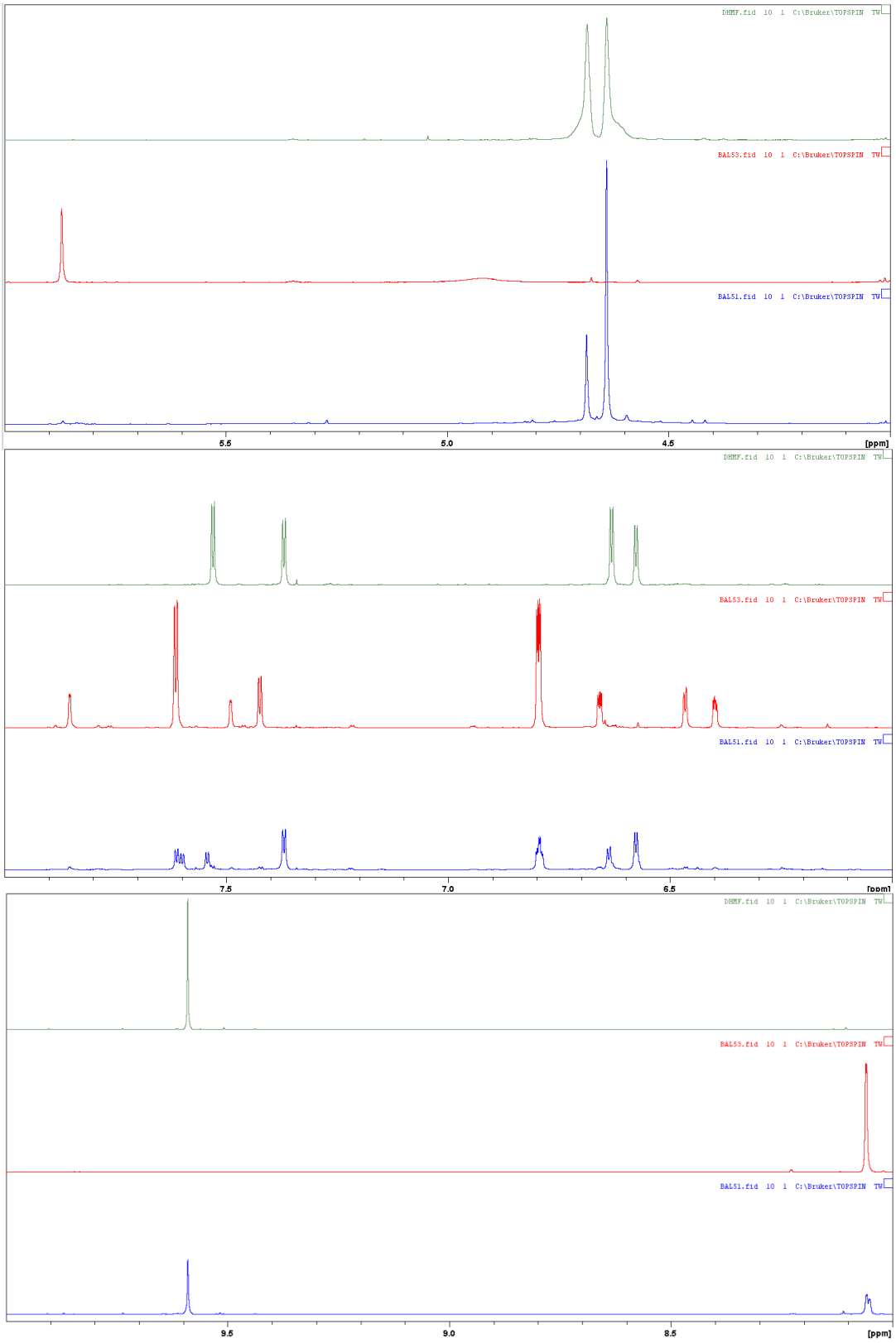
MS (EI, 100 eV): m/z (%) = 250 ([M]+, 15), 233 (43), 125 ([$C_6H_5O_3$]$^+$, 100), 69 (19), 52 (18), 51 (23), 50 (20).

HRMS (ESI): [M]+Na$^+$ calculated for [$C_{12}H_{10}O_6Na$]$^+$: 273.03696, found: 273.03699.



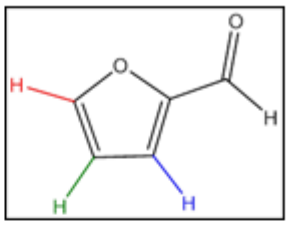


^{1}H NMR spectra for coupling reactions with HMF/Furfural substrate ratios of 100/0 (green), 0/100 (red) and 50/50 (blue)



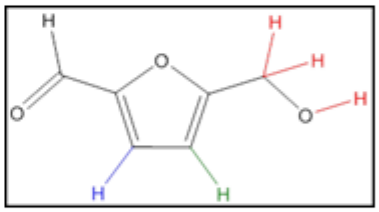
Furfural

δ (ppm)	#H	Multiplicity
9.67	1H	s
7.93	1H	br s
7.43	1H	d
6.73	1H	dd



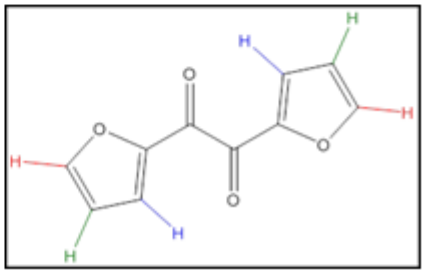
5-Hydroxymethyl furfural

δ (ppm)	#H	Multiplicity
9.59	1H	s
7.37	1H	d
6.58	1H	dt
4.62	3H	m



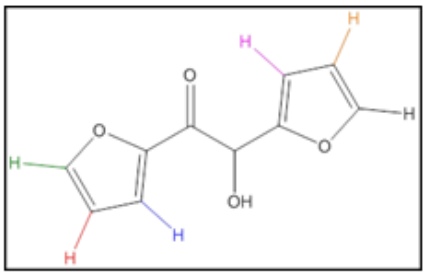
Furfural dimer dione

δ (ppm)	#H	Multiplicity
8.06	1H	dd
7.62	1H	dd
6.80	1H	dd



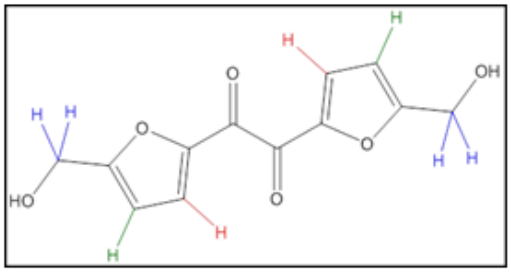
Furfural dimer hydroxyketone

δ (ppm)	#H	Multiplicity
7.85	1H	dd
7.49	1H	dd
7.43	1H	dd
6.66	1H	dd
6.47	1H	ddd
6.40	1H	ddd
5.87		s



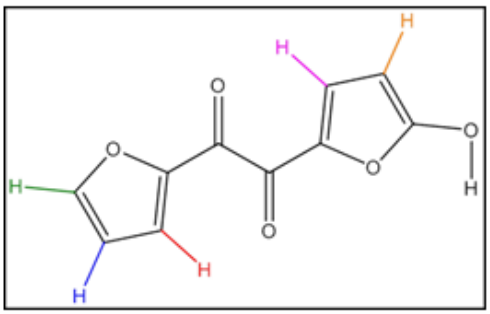
Hydroxymethylfurfural dimer dione

δ (ppm)	#H	Multiplicity
7.53	1H	d
6.63	1H	d
4.68	1H	s



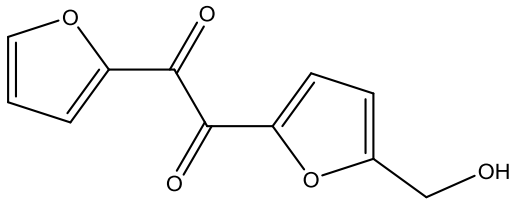
Hydroxymethylfurfural - furfural cross coupled dione

δ (ppm)	#H	Multiplicity
8.05	1H	dd
7.6	1H	dd
7.55	1H	dt
6.79	1H	dd
6.64	1H	dt



Conversions were calculated by identification of product peaks through comparison of product chemical shifts with those of substrate shifts according to substrate spectra and spectra of isolated coupled HMF products. Subsequent integration of relevant peaks yielded relative quantities of each product. The peak identifications are presented in the preceding 2 pages.

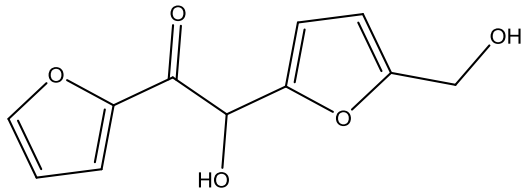
1-(furan-2-yl)-2-(5-(hydroxymethyl)furan-2-yl)ethane-1,2-dione



^{1}H NMR (500 MHz, acetone-*d6*): 4.68 ((br)s, 2H) 6.64 (dt, *J*= 3.7, 0.7 Hz, 1H) 6.79 (dd, *J*= 3.6, 1.7 Hz, 1H) 7.55 (dt, *J*= 3.6, 0.4 Hz, 1H) 7.60 (dd, 3.7, 0.7 Hz, 1H) 8.05 (dd, *J*= 1.7, 0.8 Hz, 1H)

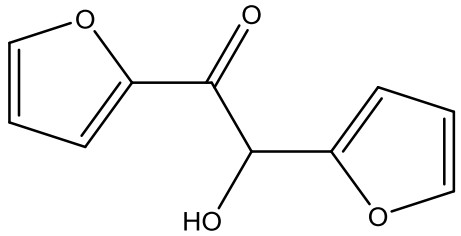
HRMS (ESI): $[M]+Na^{+}$ calculated for $[C_{11}H_8O_5Na]^{+}$: 243.0298, found: 243.0255.

1-(furan-2-yl)-2-hydroxy-2-(5-(hydroxymethyl)furan-2-yl)ethanone



HRMS (ESI): $[M]+Na^{+}$ calculated for $[C_{11}H_{10}O_5Na]^{+}$: 245.0398, found: 245.0407.

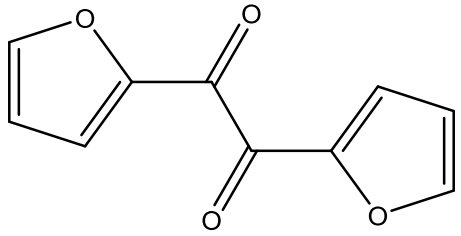
1,2-di(furan-2-yl)-2-hydroxyethanone



^{1}H NMR (500 MHz, acetone-d_6): 5.87 (s, 1H) 6.40 (ddd, *J*= 3.3, 1.8, 0.3 Hz, 1H) 6.47 (ddd, *J*= 3.3, 0.8, 0.4 Hz, 1H) 6.66 (dd, *J*=3.6, 1.7 Hz, 1H) 7.43 (dd, *J*= 3.6, 0.7 Hz, 1H) 7.49 (dd, *J*= 1.8, 0.8 Hz, 1H) 7.85 (dd, *J*= 1.7, 0.7 Hz, 1H)

HRMS (ESI): [M]+Na^+ calculated for $[C_{10}H_8O_4Na]^+$: 215.0298, found: 215.0278.

1,2-di(furan-2-yl)ethane-1,2-dione



^{1}H NMR (500 MHz, acetone-d_6): 6.80 (dd, *J*= 3.7, 1.7 Hz, 2H) 7.62 (dd, *J*= 3.7, 0.7 Hz, 2H) 8.06 (dd, *J*= 1.7, 0.7 Hz, 2H)

HRMS (ESI): [M]+Na^+ calculated for $[C_{10}H_6O_4Na]^+$: 213.0198, found:213.0161.

2.8 CONTEXT REFERENCES

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Chapter 3

BRANCHED KETONE BIOFUELS AS BLENDING AGENTS FOR JET-A1 AVIATION KEROSENE

The work presented in this chapter was completed either by the author, or under the direct supervision of the author. The work was published in December 2015 in Energy and Fuels.

Donnelly J., et al., *Branched ketone biofuels as blending agents for Jet-A1 aviation kerosene,* Energy Fuels*,* ***2016****,* 30 *(1), pp 294–301*

3.1 CONTEXT

Jet fuels require a particular set of characteristics with respect to their physical properties. The utilisation of the vast majority of biomass derived compounds without any kind of catalytic upgrading is not possible, due to the short chain lengths of these products, typically 1-6 carbon chain length. The engineering of microorganisms for the production of longer chain length molecules, has and is being attempted, however it seems likely that in the short to midterm, the most promising route to jet fuel range precursors is through the thermochemical and catalytic upgrading of short chain oxygenates, as discussed in the previous chapter.

Acetone butanol ethanol (ABE), fermentation provides a potentially sustainable and industrial scale route to production of diesel fuel precursors, when coupled with a suitable conversion technology. Anbarrassan et al. demonstrated one such conversion in a paper published in 2012 using transition metal catalysis to effect the linking of ABE molecules to produce a longer chain oxygenate.[1] These longer chain molecules however do not have the requisite low temperature properties for use as an alternative aviation fuel. The incorporation of branching into molecules is a potential route to improve their low temperature properties and potentially allow the adaptation of this promising alkylation reaction for the production of an alternative and sustainable aviation turbine fuel.[2]

With advancements in genetic and metabolic engineering it is likely that the manipulation of the bacterium *Clostridium acetobutylicum* and other bacteria will allow for the production of branched chain alcohols such as isobutanol and isoamyl alcohol, as well as ABE.[3] The incorporation of these branched analogues, of more commonly produced straight chain products, would potentially allow for a tailorable product distribution of jet fuel range molecules with improved low temperature properties.

The technique investigated here is a palladium catalysed, solvent free, low temperature (<200 °C) reaction, which was shown to be effective for the alkylation of various theoretical permutations of the ABE fermentation product mixture, incorporated branched chain alternatives, in place of n-butanol. The physical properties of the resultant product mixtures were examined and their suitability as a ‘drop in’ jet fuel alternative assessed.

This chapter is submitted in an alternative format in line with Appendix 6A of the 'Specifications for Higher Degree Theses and Portfolios' as required by the University of Bath.

The work presented in this paper was completed by the author with assistance on preliminary experiments by Mr Richard Horton. Dr. Kesavan Gopalan assisted with GC-MS analyses and a portion of the paper construction. Dr. Chris Chuck and Dr. Chris Bannister supervised the work within the paper and edited for submission.

3.2 ENERGY & FUELS PAPER

Branched ketone biofuels as blending agents for Jet-A1 aviation kerosene

*Joseph Donnelly,[a] Richard Horton,[b] Kesavan Gopalan,[b,c] Chris D. Bannister[c] and Christopher J. Chuck[b]**

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KEYWORDS

Butanol, Aviation, Biofuel, Biorefinery, Kerosene, Jet

3.3 ABSTRACT

In this investigation a range of ketone biofuels produced from the alkylation of isoamyl alcohol and isobutanol were examined as potential blending agents with Jet A-1 aviation kerosene. The fuels were synthesised under solvent-free conditions using a Pd/C catalyst with K_3PO_4, previously reported for the alkylation of acetone, butanol, ethanol (ABE) fermentation mixtures. Reasonable yields and selectivity were achieved for branched alkylation products with up to 61 % produced from isoamyl alcohol and 64 % from isobutanol. The key aviation fuel properties of the mixtures were tested unblended and in 50% and 20% blends with Jet A-1 aviation kerosene. The freezing point of the fuels were all found to be below the required -47 °C irrespective of blend or the temperature of the reaction. The energy density of the unblended fuels ranged between 30.4-41.36 MJ/kg depending on the temperature of the reaction and whether remaining alcohols were removed. While this is below the HHV of the Jet A-1 used (45.69 MJ/kg) the energy density of the 50% and 20% blends were more suitable with the isoamyl alcohol derived fuels having a maximum HHV of 44.31 MJ/kg at 50% blending and 44.99 MJ/kg at 20% blend with Jet A-1. The fuels derived from isoamyl alcohol produced above 140 °C were found to satisfy the flash point criterion (>38 °C) of the Jet A-1 specification, though the isobutanol derived fuels did not, producing fuels with flash points between 33 °C and 35 °C. The kinematic viscosity of the fuels were also tested at -20 °C. Unblended only a few of the fuels analysed met the maximum viscosity requirement at -20 °C of 8 mm^2 s^{-1}, though this fuel property was improved substantially on blending with jet fuel. This work demonstrates that ketones produced from isoamyl alcohol through a simple alkylation have the potential to be used as blending agents with Jet A-1.

3.4 INTRODUCTION

The aviation industry contributes approximately 2% of anthropogenic greenhouse gases and as such is under increasing global pressure to reduce carbon emissions through increasingly strict targets.[1] The development of renewable aviation biofuels, suitable for blending with aviation kerosene is therefore a key priority. Suitable aviation biofuels must possess a number of characteristics such as a high energy density, good atomisation, an ability to be relit at altitude though a low explosive risk on the ground, a suitably low viscosity, an extremely low freezing point and good chemical stability. The fuel should also be reasonably non-toxic and be widely available.[2-6]

While the hydroprocessing of lipids offers a suitable route to hydrocarbons, edible oils compete with arable land, promote deforestation and are not produced in suitable quantities. A more promising route to second generation biofuels is *via* fermentation of lignocellulosic biomass.[7] While the technology to produce second generation bioethanol is becoming established, the low energy density and high water affinity of ethanol have led to the development of alternatives such as n-butanol,[8] isoamyl alcohol and isobutanol.[9, 10] Despite the increased energy density of these compounds over ethanol, the water affinity, low flash point and low boiling point make these unsuitable for aviation without further upgrading.

Recently the alkylation of butanol, with acetone and ethanol, has been investigated as a potential method for the production of longer chain components more suitable for the current fuel market.[11] ABE products comprise both the nucleophilic α-carbons of the acetone and the electrophilic α-carbons of the alcohol. These paired functionalities enable the construction of higher alkanes from two, three and four-carbon precursors by the alkylation of acetone with the electrophilic alcohols. The alkylation results in the formation of long-chain ketones in the C_5 to C_{11} range, which may be deoxygenated to paraffins suitable as components in gasoline.[12]

Guillena and co-workers investigated the double alkylation of acetone under transition-metal catalysed conditions.[13, 14] They hypothesised that two possible side reactions could occur in a transition metal-catalysed alkylation of acetone with primary alcohols; (i) self-condensation of the alcohol to the corresponding aldehyde (Guerbet reaction)[15] and (ii) combination of acetone to form diacetone alcohol, mesityl oxide, and other products.[16] Other work on the conversion of ABE includes their catalytic

upgrading to ketones using hydrotalcite (HT) supported copper(II) and Pd(0) catalysts with integration of isopropanol from engineered strains of acetobutylicum.[17] The sequential condensation of butanol to Guerbet alcohol and subsequent alkylation of acetone by the Guerbet product has been demonstrated using HT supported ruthenium catalysts,[18-21] though the corresponding ketones were only obtained in a 20 % yield. A bimetallic HT supported Pd/Ru catalyst was shown to offer modest improvement on this yield. Where butanol was used as the reaction medium yield of the ketone was shown to increase to 58%.[17]

However, the straight chain ketones produced from the upgrading of these ABE mixtures have too high freezing points to be considered for aviation, while the derived hydrocarbons are only suitable for gasoline applications due to the low flash point. In this investigation the suitability of producing ketones with superior low temperature properties was examined by introducing branching into the ketone chain. This was achieved through the alkylation of isobutanol and isoamyl alcohol with acetone. The key fuel parameters of both the unpurified alcohol/ketone product mixtures and the mixtures after removal of remaining alcohol were assessed.

3.5 EXPERIMENTAL

3.5.1 Materials

All chemicals (isoamyl alcohol >98%, isobutanol >99%, acetone >99.9%, potassium phosphate tribasic >98%, 5 wt% Pd/C) were purchased from Sigma Aldrich and used without further purification.

3.5.2 Methods

3.5.2.1 Alkylation reactions

To a 350 mL stainless steel stirred pressure vessel (Parr Instruments, USA) was added 5.67g Pd/C (5 wt% Pd) and 64.40 g K_3PO_4. To this was then added 1.782 mol of alcohol substrate with 0.891 mol acetone. The vessel was then sealed and stirring commenced at 320 rpm. Heating was ramped to 120 °C, 140 °C or 160 °C at a rate of 3 °C/min. The reaction was allowed to proceed for 20 hours. On reaction, the contents of the reactor were then filtered twice to remove all heterogeneous catalyst and base. Reactions were undertaken in triplicate and the standard deviation calculated.

Reaction profiles were obtained by analysing aliquots obtained from the stirred pressure vessel, using GC-MS. The GC-MS used was an Agilent 7890B Gas Chromatograph coupled to an Agilent 5977A inert MSD with Triple Axis Detector. The machine was fitted with a DB-FFAP nitroterapthalic-acid-modified polyethylene glycol column of high polarity and a He mobile phase (flow rate: 1.2 mL min^{-1}). Analysis temperature ranged from 40 °C – 250 °C with a ramp rate of 20 °C/ min and temperature plateau of 5.5 min before cooling. A portion of the fuel samples (approximately 50 mg) was initially dissolved in 10 mL dioxane and 1 µL of this solution was loaded onto the column, pre-heated to 150 C. This temperature was held for 5 min and then heated to 250 °C at a rate of 4 °C min^{-1} and then held for 2 min. The% areas, used as a quantitative method of analysis were calculated from the GC–FID chromatograph and compared against a dodecane internal standard.

3.5.2.2 Removal of Alcohols

For isoamyl alcohol mixtures, remaining alcohols were removed via vacuum distillation by removal of a mid-boiling fraction at 70 °C (condenser inlet temperature) under a reduced pressure of 112 mmhg. The remaining alcohols in the unpurified mixture were predominantly found to be unreacted alcohol substrate by ^{1}H NMR. The other fractions (lower and higher boiling) were determined to contain negligible quantities of alcohols by ^{1}H NMR and were recombined to constitute 'alcohol free' fuels.

An analogous process was carried out for the isobutanol mixtures however the removed fraction was obtained at 50 °C (condenser inlet temperature), and a pressure of 112 mmhg.

3.5.2.3 Fuel Properties

Viscosities were determined in accordance with ASTM D445 using a Canon-Fenske capillary kinematic viscometer. Temperature modulation was achieved using a refrigeration unit. Samples within the viscometer were allowed to rest at the required temperature for a minimum of 5 minutes prior to viscosity measurement to allow temperature equilibration. The standard error was found to be lower than ±0.073 mm^2s^{-1} at -20 °C, ±0.128 mm^2s^{-1} at 20 °C and ±0.100 mm^2s^{-1} at 40 °C.

Melting points of the fuels were determined visually by cooling of 1.5 cm^3 vials of the samples in a low temperature freezer, and periodically checking to see if the melting point had been surpassed. The samples were allowed to rest at each temperature for a minimum of 10 minutes in order to allow equilibration of sample and freezer temperatures. All melting points tested were found to have no more than 1 °C standard experimental error.

Energy content of fuels was determined in accordance with ASTM D3338 using an IKA C1 automatic bomb calorimeter. Approximately 0.3 g of each sample was used. The error of measurements was found to be <0.5 %.

Flash points of each sample were determined in accordance with ASTM D56/IP 170 using a Stanhope-Seta 99880-0 Flashcheck, tag, closed cup flash point machine. All flash point measurements were measured to an accuracy of ±1 °C or better.

3.6 Results and Discussion

The products of the isoamyl alkylation (IAP) and isobutyl alkylation (IBP) were synthesised according to literature precedent.[11] The component products were determined by GC-MS analysis. In each instance, alcohol and acetone substrates were used in a 2:1 molar ratio, with the intention that a double alkylation product in the carbon range $C_{11\text{-}15}$ would be achieved.

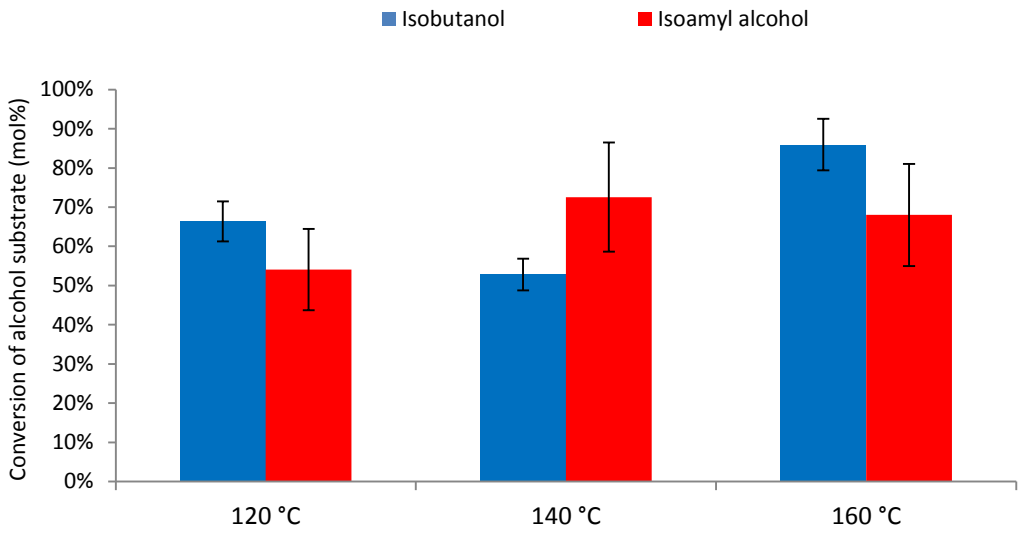


Figure 3.6-1: Conversion of starting alcohol substrates for reactions at varying temperatures. Error bars are given as standard deviation (n=3).

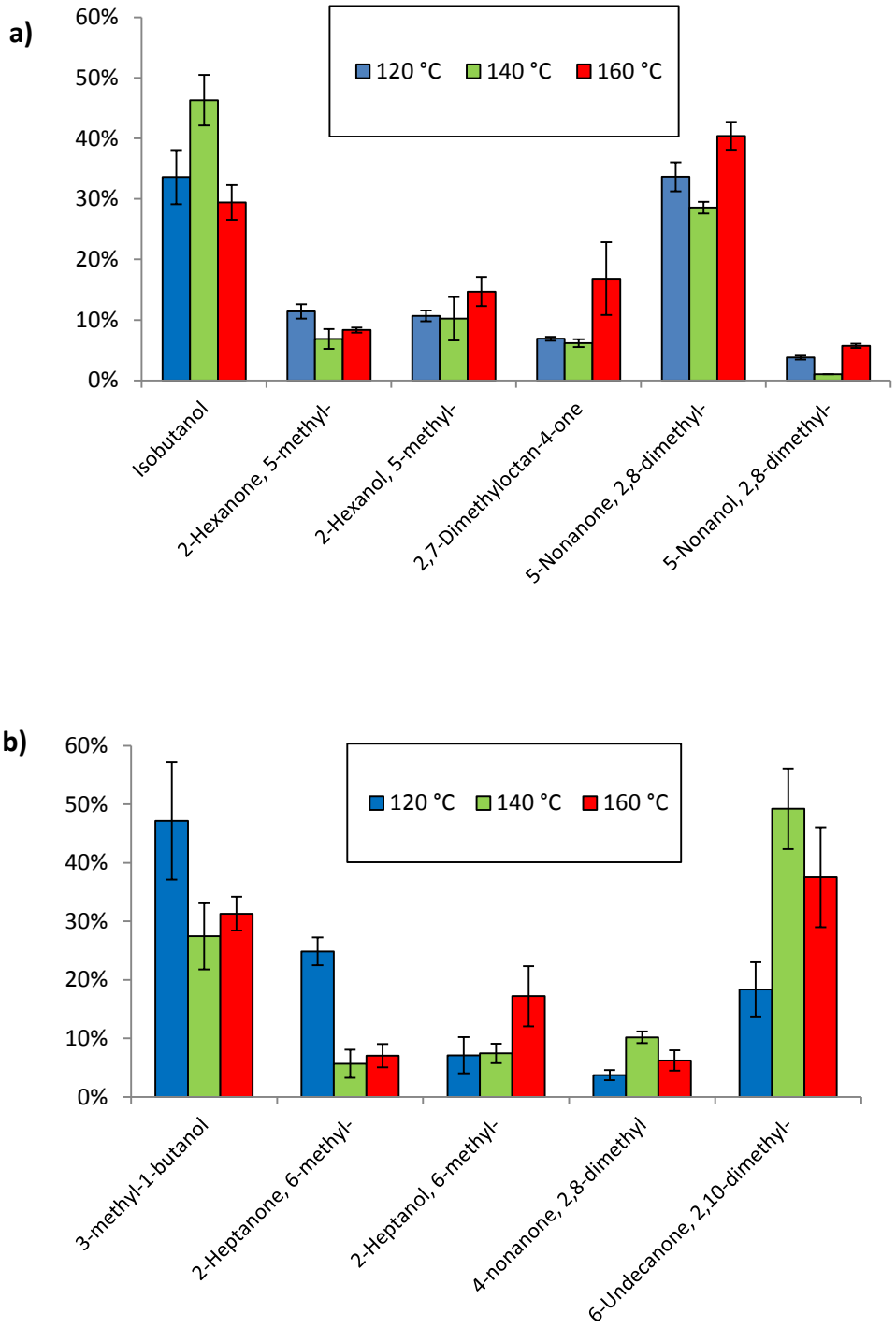
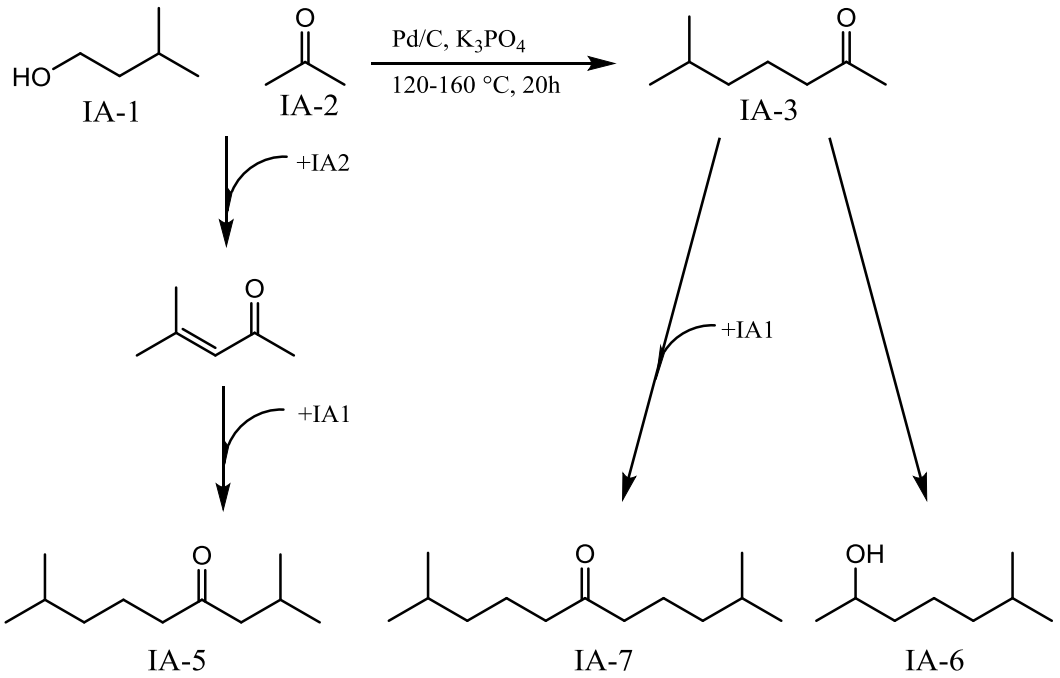


Figure 3.6-2: Product distribution of the branched alcohol reactions at 120 °C, 140 °C and 160 °C, 20 h, 0.3 mol% Pd catalyst. Where a) shows isobutanol-acetone alkylation reactions and b) shows the reaction of isoamyl alcohol. Standard deviation (n=3) are presented

Variation of product mixture composition at different reaction temperatures was observed (Figure 3.6-2). In the case of isobutanol-acetone alkylation, conversion of isobutanol to an alkylated product is 66%, 54% and 71% for reaction temperatures 120, 140 and 160 °C, respectively, showing a lower conversion at the mid-temperature than at lower or higher temperatures. With increasing temperature, the quantity of the single alkylate, 5-methyl-2-hexanone (as a proportion of non isobutanol products), decreases approximately linearly with increasing temperature. This single alkylate constitutes 17 % of products at 120 °C and 10 % at 160 °C. The opposite trend is observed for 2,7-dimethyl-4-octanone which depends on the initial self-condensation of acetone to form mesityl oxide, which increases with increasing temperature. It is thought that at the higher temperature there is relatively rapid self-condensation of the acetone to form mesityl oxide, which is then available for further alkylation with the available isobutanol. At lower temperatures, the self-condensation of acetone is less favoured, resulting in a longer residence time of acetone in the reaction solution, and thus greater proliferation of the acetone-isobutanol alkylation.

In the case of isoamyl alcohol products conversion of the alcohol substrate is 54 %, 73 % and 68 % for 120, 140 and 160 °C, respectively. At the lower temperature, there is a notably lower proportion of double alkylate products (34% of alkylate products) formed relative to shorter chain, single alkylates such as the single alkylate, 6-methyl-2-heptanone (46% of alkylate products). At the higher temperatures the product distribution is shifted towards double alkylation with 68 % and 55 % 2,10-dimethyl-6-undecanone at 140 and 160 °C respectively as opposed to 34 % at 120 °C (excluding alcohol substrate). Conversion to alkylates which are then reduced to alcohols appears to be favoured to a small degree at higher temperatures.

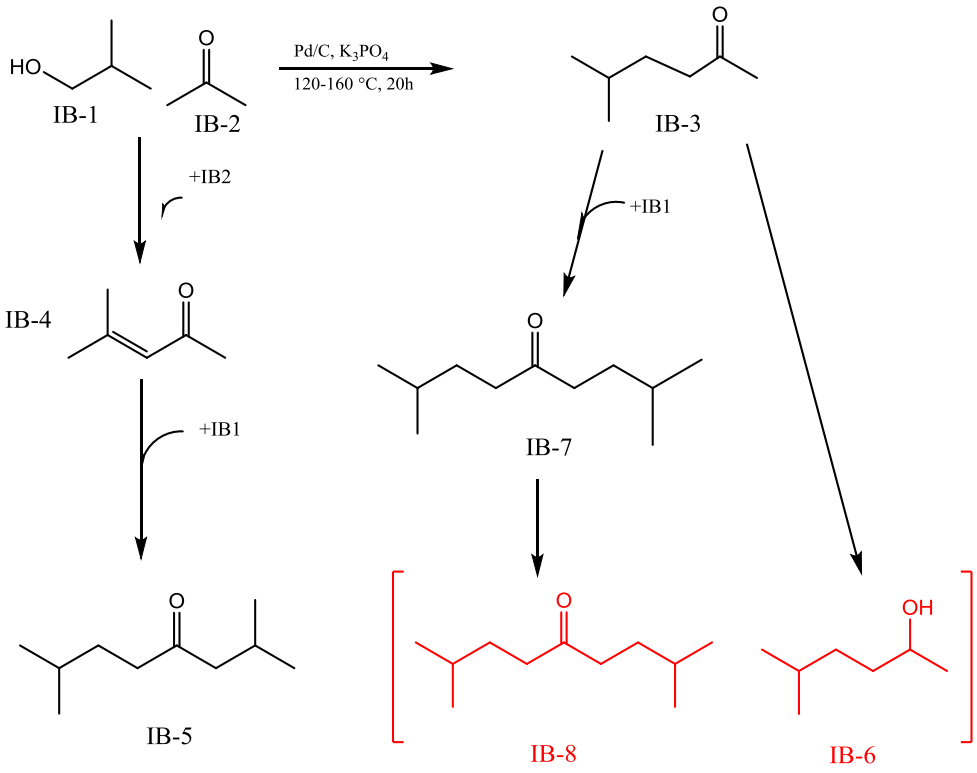
Between the two alcohol substrates, conversion to double alkylates is marginally favoured at higher temperatures, however the self-condensation of acetone to a mesityl oxide intermediate inhibits selectivity for the double alcohol-acetone coupled product.



GC-MS certainty scores for each compound

IA #	% Probability
1	substrate
2	substrate
3	82
4	inferred
5	62
6	66
7	49

Figure 3.6-3: Alkylation of isoamyl alcohol with acetone. Formation of side product (IA5) is shown competing with the formation of products IA3, IA6 and IA7.



GC-MS certainty scores for each compound

IA #	% Probability
1	substrate
2	substrate
3	79
4	inferred
5	67
6	51
7	71
8	55

Figure 3.6-4: Alkylation of isobutanol with acetone. Similarly to scheme 1, the self-coupling of acetone and subsequent production of product IB5 competes with production of products IB3, IB6, IB7 and IB8. The presence of products highlighted in red require confirmation through further analysis as it is unclear how they are formed.

96IAIsoamyl alcohol does not exhibit the same pattern of higher efficiency at lower temperatures with respect to alkylation with acetone under the conditions used, but rather at 140 °C. At this temperature there is a marked propensity for the formation of the double alkylation product, 2,10-dimethyl-6-undecanone (IA7), which accounts for 49% of the final product mixture, compared to just 18% and 38% for the reactions run at 120 °C and 160 °C respectively. Potentially the increase in temperature from 120 °C to 140 °C allows for a faster oxidation of the alcohol to the corresponding aldehyde, allowing the alkylation reaction to proceed, however, when the temperature is increased above 140 °C to 160 °C, the reduction of the ketone to the corresponding alcohol is expedited, effectively halting further alkylation.

To assess the efficiency of the catalyst the reaction profile of the alkylation reactions were determined. The reaction profile of the isoamyl alcohol reaction at 140 °C is given in Figure 3.6-5. From the reaction profile, it is evident that most of the conversion of isoamyl alcohol occurs within the first four hours. As expected, the reaction appears to proceed sequentially through the initial coupling of acetone and isoamyl alcohol to produce 6-methyl-2-heptanone, IA3, which is then available to couple with another isoamyl alcohol molecule to yield the double alkylation product, 2,10-dimethylundecan-6-one (IA7). Whilst the production of these two ketones occurs with obvious interdependence, the concurrently occurring reaction to produce 2,8-dimethylnonan-4-one (IA5) does not show dependence on any other product. This suggests that acetone self-couples to produce 4-methylpentan-2-one, IA4, before coupling with isoamyl alcohol rather than acetone coupling with 6-methyl-2-heptanone. The production of the alcohol derivative, 6-methyl-2-heptanol is presumably due to the reduction of the ketone, and proceeds at the greatest rate between 1 and 2 hours, when there is the greatest availability of the ketone. Catalyst recycle tests suggest that only a minimal amount of activity is retained (data not shown). It is therefore likely that it is a combination of the depletion of acetone and catalyst deactivation that causes conversion rate to slow dramatically after 4 hours.

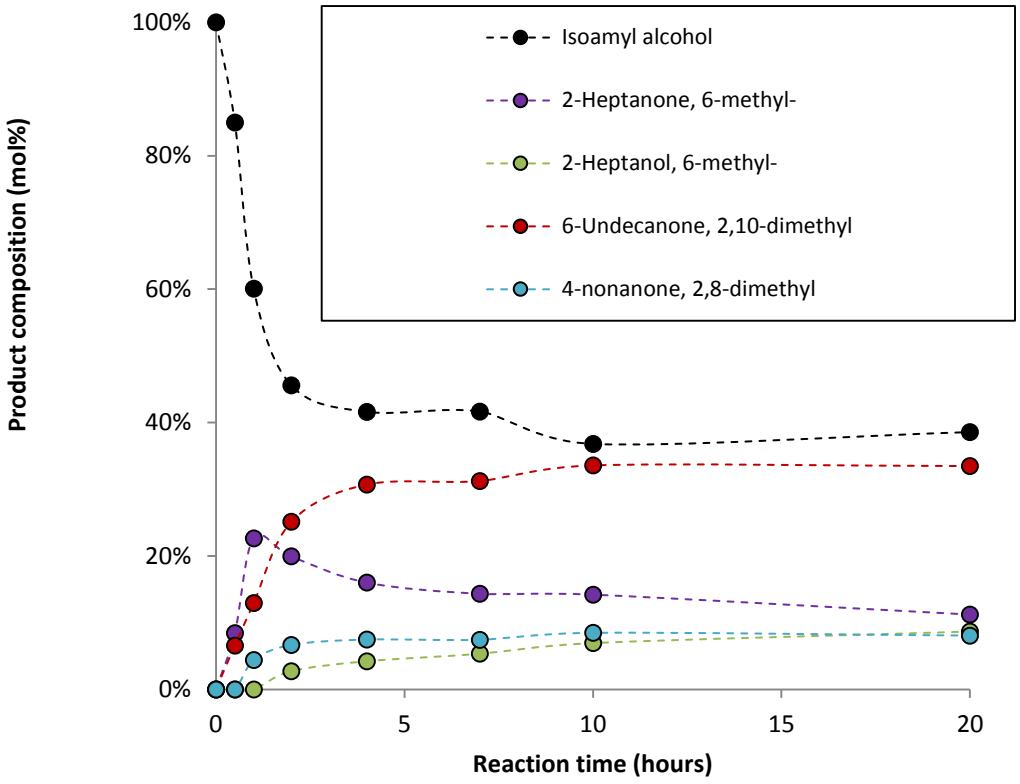


Figure 3.6-5: Reaction profile for the alkylation of isoamyl alcohol at 140 °C, in a stirred autoclave. Isoamyl alcohol 1.8mol, acetone 0.9mol, K_3PO_4 0.3mol,0.3wt% Pd (5.783g 5wt% dry basis Pd/C) over 20 hours.

All remaining acetone was removed from the resulting fuel mixtures through distillation resulting in the isoamyl product (IAP) and isobutanol product (IBP) fuels. These ketone/alcohol mixtures were blended with aviation kerosene (Jet A-1) and the fuel properties examined.

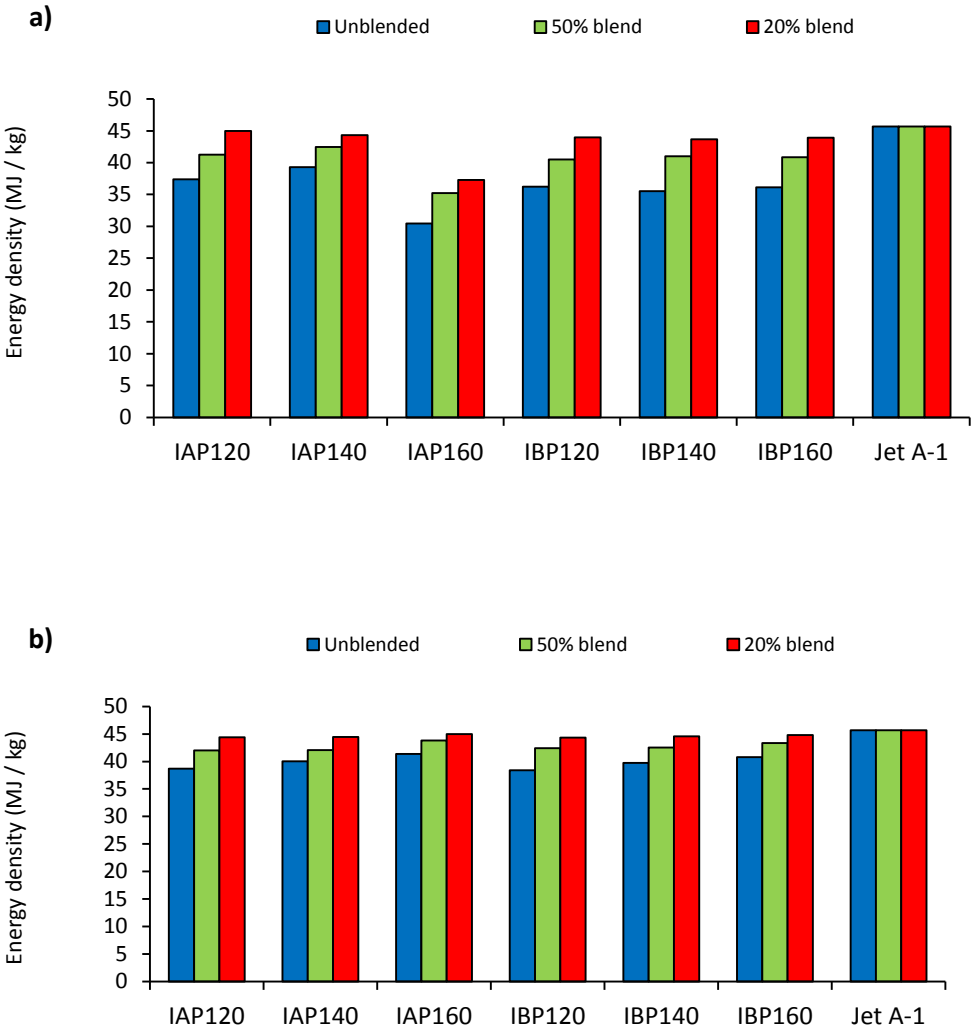


Figure 3.6-6: Higher heating values of the isoamyl (IAP) and isobutyl (IBP) fuel products and their blends (100%, 50% and 20% with Jet A-1) where a) is the fuel mixtures including the alcohols b) shows the HHV of the fuel blends where the parent alcohols have been removed. The number associated with each fuel corresponds to the temperature at which the reaction to produce each was conducted at.

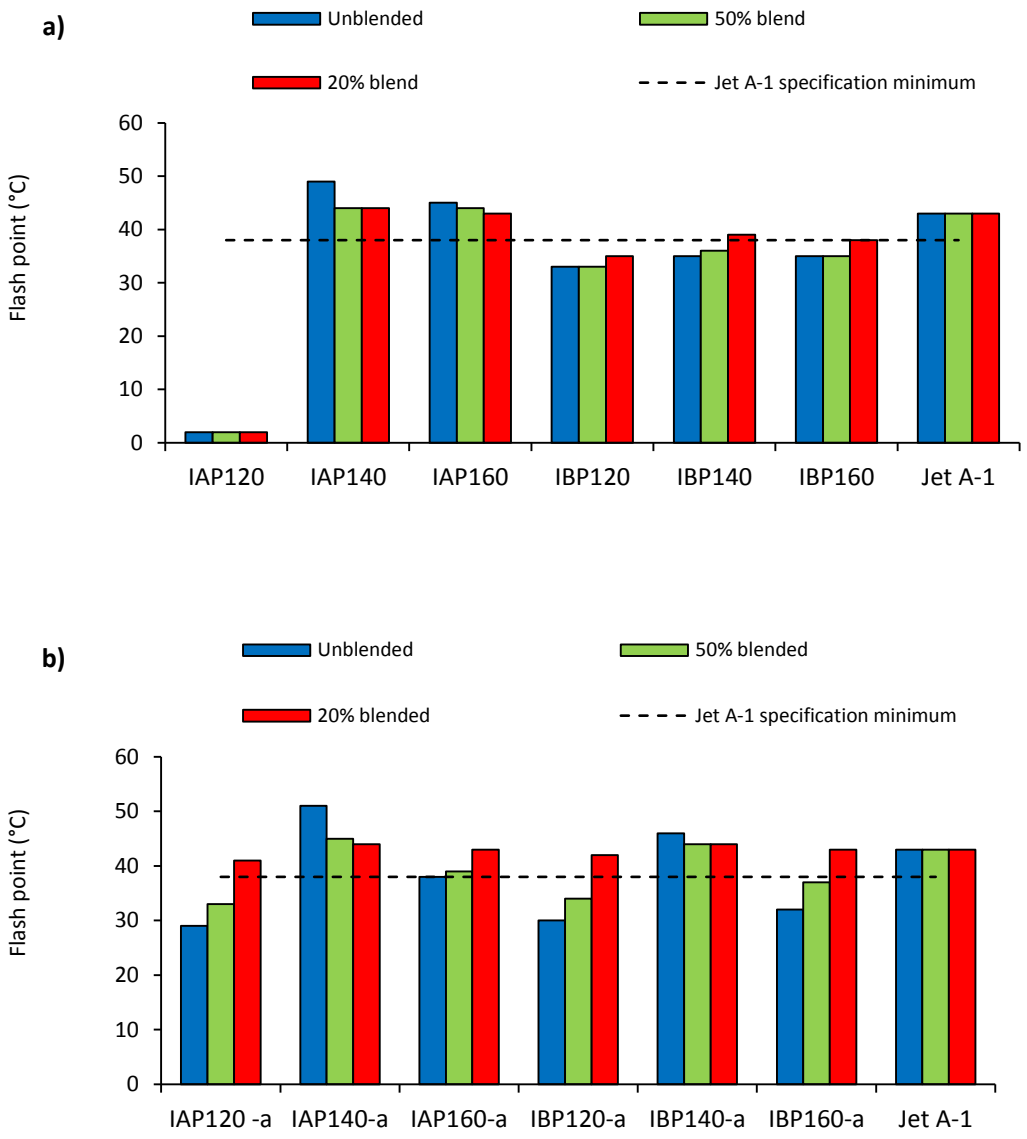


Figure 3.6-7: Flash point of the isoamyl (IAP) and isobutyl (IBP) fuel products and their blends (100%, 50% and 20% with Jet A-1) where a) is the fuel mixtures including the alcohols b) shows the flash point of the fuel blends where the parent alcohols have been removed

The flash point temperature of fuel blends that showed a change after removal of alcohols were generally increased. It is likely that the process of an aqueous wash served to remove residual acetone in the IAP120 fuel, accounting for the much increased flash point temperature. This is due to acetone possessing a very low flash point temperature of -20°C and requiring only small quantities (2.8 vol.%) with air for the formation of a combustible fuel/air mixture.

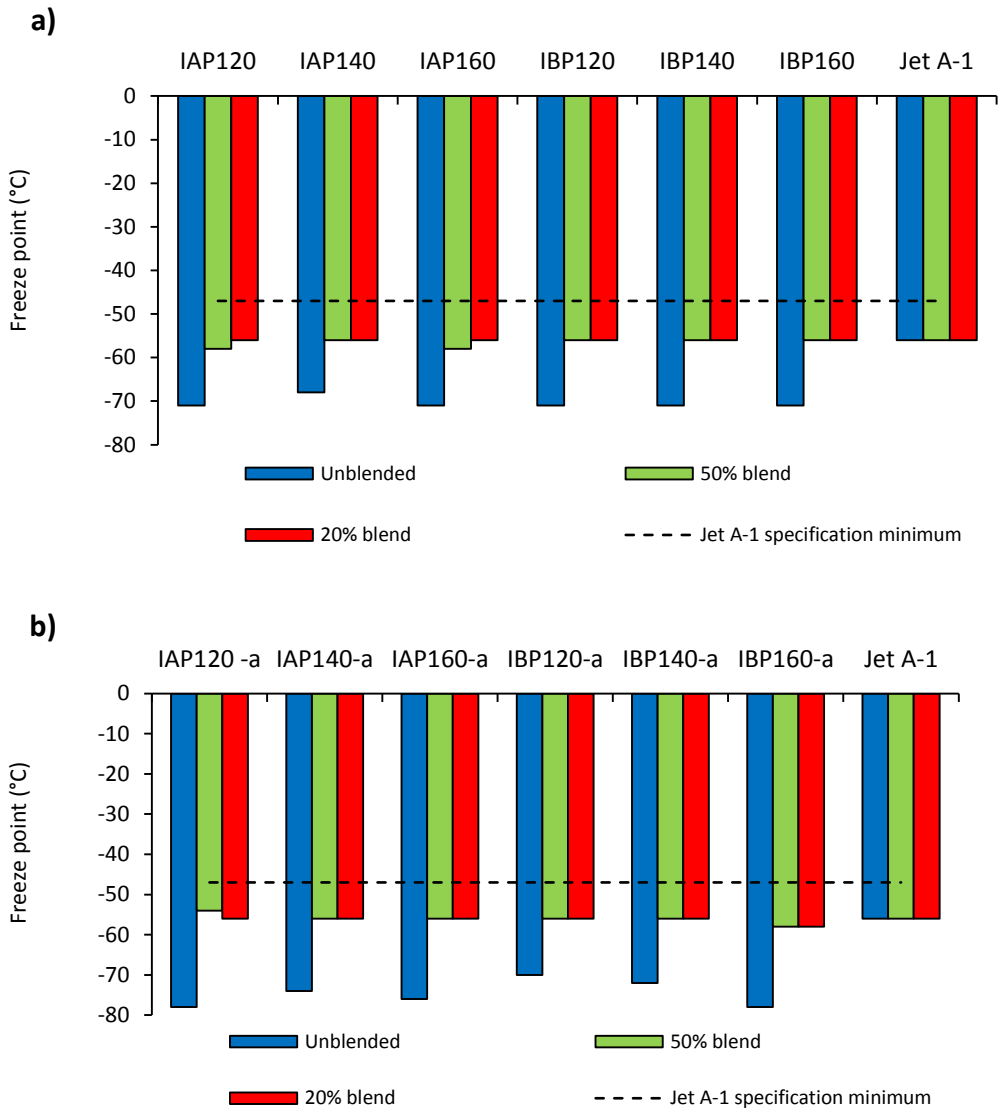


Figure 3.6-8: Freeze point of the isoamyl (IAP) and isobutyl (IBP) fuel products and their blends (100%, 50% and 20% with Jet A-1) where a) is the fuel mixtures including the alcohols b) shows the freeze point of the fuel blends where the parent alcohols have been removed

The gravimetric energy density is an important metric, as it directly affects the efficiency obtained by using a particular fuel. The Jet A-1 specification stipulates a minimum lower heating value (LHV) of 42.8 MJ/kg. The higher heating value of Jet A-1 used in this study was found to be 45.69 MJ/kg. Whilst it has become common practice to measure the HHV and quote this as the LHV due to the 'negligible' quantities of water contained within conventional hydrocarbon fuels, it is the opinion of the author that this is unacceptable for the analysis of generally more hygroscopic oxygenated fuels. Therefore, the HHV of each fuel is given in this investigation. The

standard method of adiabatic bomb calorimetry was used and values are comparable with values quoted in the literature, which have been obtained through adiabatic bomb calorimetry.

Of the two alcohol derived fuels, isoamyl alcohol derivatives achieve the greatest energy density, with IAP140 without removal of substrate alcohol, exhibiting a HHV of 39.28 MJ/kg, corresponding to the higher level of double alkylated species (Figure 3.6-6). When the remaining alcohol was removed, IAP160 exhibited a slightly higher HHV of 41.359 MJ/kg. The highest value shown by isobutanol derived fuels without removal of substrate alcohol is that of IBP120 at 36.21 MJ/kg however when the alcohol was removed, IBP160 exhibited the highest HHV at 40.760 MJ/kg. When substrate alcohols are removed, a positive correlation between reaction temperature and product mixture gravimetric energy content is observed. Removal of the alcohol substrates, in all cases, acts to increase the energy density of the product mixtures.

The closed cup flash point is a key metric with aviation fuel, the Jet A-1 specification stipulates that this temperature should be higher than 38 °C. The Jet A-1 used in this investigation was found to have a flash point of 43 °C (Figure 3.6-7). Of the synthetic, alcohol derived fuels, IAP140 and IAP160 were the only fuels to satisfy this criterion exhibiting flash point temperatures of 49 °C and 45 °C respectively. IAP120 exhibited a flash point of 33 °C when unblended with Jet A-1, rising to 36 °C at a 20 % blend level. Of the IBP fuels, IBP120 exhibited the lowest value, of 33 °C, with IBP140 and IBP160 both possessing flash point temperatures of 35 °C. IBP fuels do not therefore, satisfy the flash point criterion of the Jet A-1 specification. Upon removing the parent alcohols the flash point is increased for the majority of the samples, particularly in the case of IAP120, where unreacted substrate was depressing the flash point of the product mixture to below room temperature however, after substrate removal, the flash point was only increased to 29 °C. IBP140 without removal of remaining substrates did not satisfy the flash point criterion for jet fuel, however with removal it surpasses the required value, exhibiting a flash point of 46 °C for the unblended product mixture.

Excitingly, both the fuels with and without alcohols had extremely low freezing points with the unblended fuels all having a melting point between -68 °C and -78 °C (Figure 3.6-8). This is a significant improvement on the straight chain ketones that fall between -43 °C – 14 °C (Table 3.6-1: Fuel properties of straight chain ketone and alkane derivatives, the flash points and melting points were obtained from the Scifinder database,22 kinematic viscosity was experimentally determined.). This dramatic improvement in the low temperature properties, is presumably attributable

to the presence of branching in the constituent molecules. This branching acts to disrupt intermolecular interactions and thus suppresses the melting point temperature improving the cold flow characteristics.

Table 3.6-1: Fuel properties of straight chain ketone and alkane derivatives, the flash points and melting points were obtained from the Scifinder database,22 kinematic viscosity was experimentally determined.

Fuel	**Flash Point (°C)**	**Melting Point (°C)**	**Kinematic viscosity @ -20°C (mm^2s^{-1})**
6-Undecanone	88	14	solid
4-Nonanone	62	-16	solid
2-Heptanone	41	-42	2.09
Undecane	62	-26	4.02
Nonane	31	-53	1.98
Heptane	-4	-91	1.24

The kinematic viscosity of the novel fuels was measured at -20 °C, 20 °C and 40 °C (figure 3.4-9 & 3.4-10). The viscosity of the unblended IAP fuels is significantly above the minimum specified at -20 °C in the Jet A-1 specification. IAP140 exhibits the highest viscosity having a kinematic viscosity of 31.7 mm^2s^{-1}, with IAP160 slightly less viscous at 21.3 mm^2s^{-1} and IAP 120 less viscous again with a viscosity of 11.3 mm^2s^{-1}. This trend of varying viscosity reflects pattern of substrate conversion to higher molecular weight products.

In the case of Isoamyl alcohol, a significant reduction in the viscosity of product mixtures was achieved by removal of remaining alcohol substrate, with IAP140 and IAP160 showing a reduction in viscosity of approximately 15$mm^2\,s^{-1}$. Upon blending with jet fuel, an expected suppression of viscosity was observed, with values gravitating towards that of Jet A-1.

The opposite relationship with conversion is observed in the viscosities of the three IBP mixtures, with IBP120, which shows the highest conversion to the higher MW products, exhibiting the lowest low temperature viscosity of the three fuels, with a viscosity of 12.6 mm^2s^{-1} compared to those of IBP140 and IBP160 with viscosities of 16.8 mm^2s^{-1} and 16.4 mm^2s^{-1} respectively. Whilst IBP120 exhibits a lower viscosity than its higher reaction temperature equivalents, it is still well above the maximum allowed viscosity in the Jet A-1 standard.

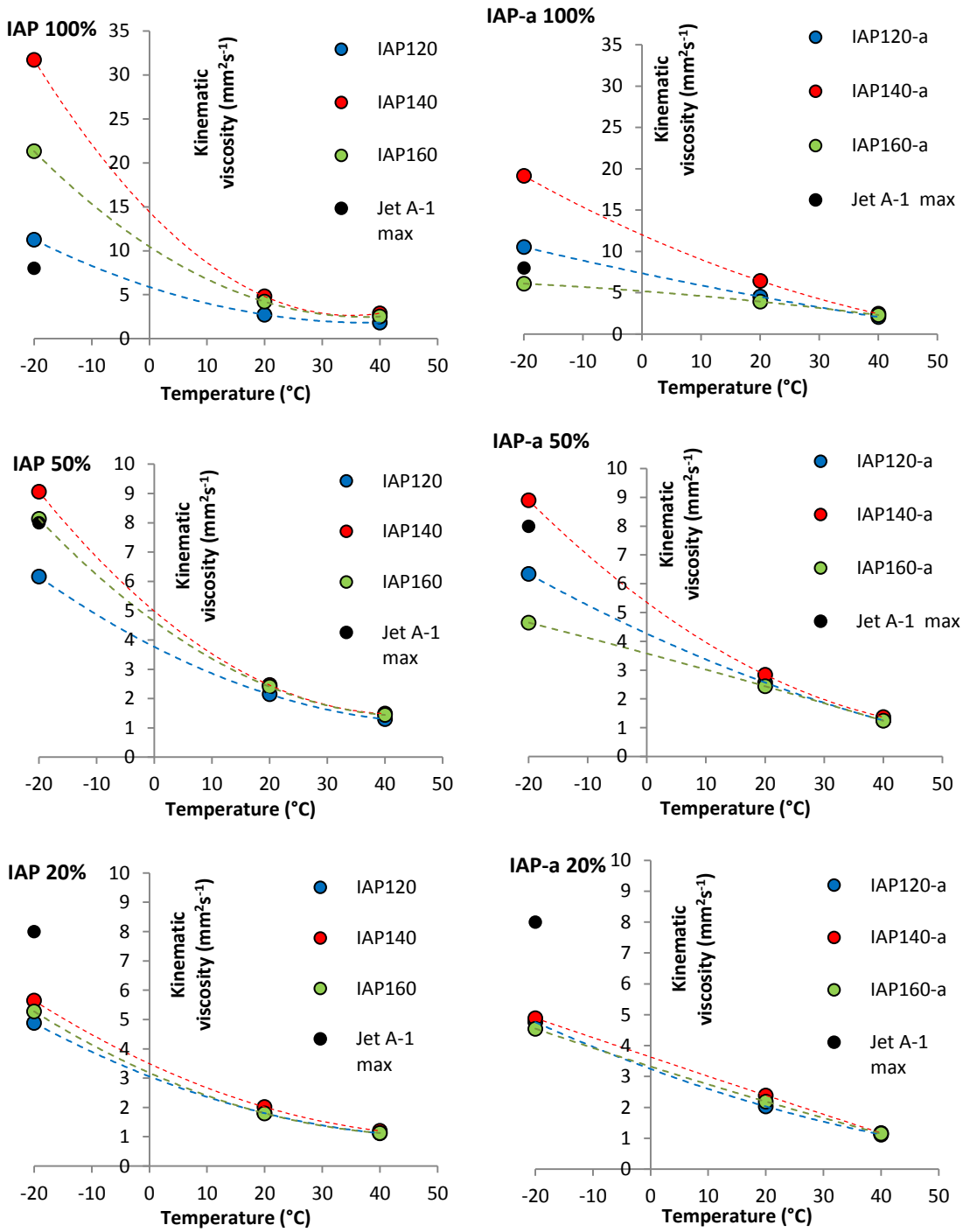


Figure 3.6-9: Kinematic viscosity of the isoamyl products (IAP) and the isoamyl fuel products with the alcohols removed (IAP-a), and their blends (100%, 50% and 20% with Jet A-1) in the temperature range -20 °C – 40 °C.

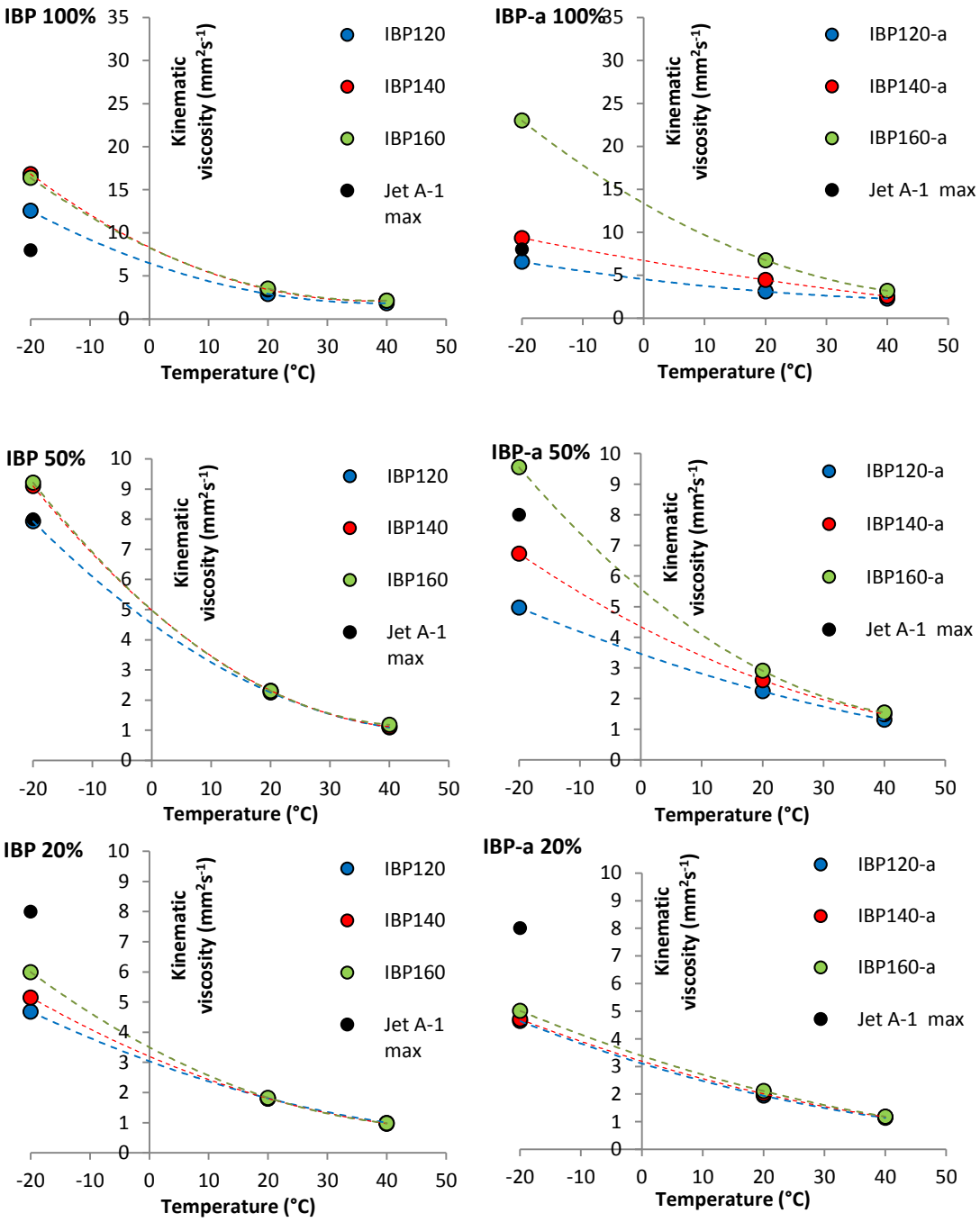


Figure 3.6-10: Kinematic viscosity of the isobutyl products (IBP) and the isobutyl fuel products with the alcohols removed (IBP-a), and their blends (100%, 50% and 20% with Jet A-1) in the temperature range -20 °C – 40 °C.

With unreacted alcohols left in situ, these fuels exceed the maximum allowed viscosity at -20 °C, arguably the maximum value for jet fuel is descriptive of conventional aviation kerosene, and that a slightly higher viscosity would not have a substantial detrimental effect on performance. Issues with pump wear and maintenance would have to be addressed as well as optimising fuel atomisation within the engine, however these should not be such great challenges so as to preclude the use of otherwise suitable aviation fuels. Alternatively the viscosity can be reduced by blending. The kinematic viscosity of all the fuels tested was reduced to between 7-9 $mm^2\ s^{-1}$ at the 50% blend level, while at a 20 % blend level, all the product mixtures satisfy the Jet A-1 criterion. Where remaining alcohols are removed however, IAP160 and IBP120 were observed to satisfy the viscosity criterion for jet fuel, without blending and all fuels except IBP160 showed a reduction in viscosity at -20 °C.

3.7 CONCLUSIONS

The solvent-free alkylation of branched alcohols with acetone resulted in complex mixtures of branched ketone fuels. These fuels were demonstrated to have superior low temperature properties in comparison to the straight chain ketones or the straight chain hydrocarbon derivatives and as such were deemed suitable for use as blending agents in aviation fuel. The conversions observed with the system used ranged between 54-73% for isoamyl alcohol derived products and 53-86% for isobutanol derived products with the Pd/C catalyst found to deactivate entirely after two uses. The energy density of isoamyl alcohol derivatives was found to be up to 39.3 MJ/Kg whilst isobutanol derivatives possess energy densities up to 36.1 MJ/Kg, while this is lower that the allowable specification with blending this was increased substantially. The flash point temperatures were found to be between 44 °C and 49 °C for isoamyl alcohol derivatives, and slightly lower for isobutanol derivatives with values between 35 °C and 39 °C. Kinematic viscosities exhibited by the novel fuels were higher than the specification maximum for Jet A-1, exhibiting values of between 11.26 mm^2s^{-1} and 31.73 mm^2s^{-1} for isoamyl alcohol derivatives and between 12.56 mm^2s^{-1} and 16.84 mm^2s^{-1} for the isobutanol products. Removal of the parent alcohols from the fuel mix improved both the kinematic viscosity and flash points of the fuels.

3.8 ACKNOWLEDGEMENTS

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Chapter 4

ASSESSMENT OF LIQUID PHASE PYROLYSIS FOR THE PRODUCTION OF A HYDROCARBON TRANSPORT FUEL FROM PISTACHIO HULL WASTE STREAM

4.1 INTRODUCTION

One of the most promising sources of biofuel to date is the thermal transformation of lignocellulosic biomass from either purpose grown energy crops, or alternatively forestry and agricultural residues and food production industry by-products and waste streams.[1-4] In this investigation a food industry waste stream, pistachio hulls provided by the Wonderful™ snack company, were assessed as a feedstock for the production of a liquid transport fuel.

The soft outer shell of pistachio nuts are removed during processing and creates a considerable waste stream for which there is currently little commercial value. In 2013, there was 917,000 metric tonnes of pistachios produced globally.[5] Approximately 18% of the pistachios mass is made up of the soft outer shell giving a potential feedstock of 165,000 tonnes available for conversion into biofuel. Currently, this waste is used for co-firing at coal fired power stations, a relatively inefficient (and non-profitable) use of the energy available. The pistachio waste used in this investigation originated in California, USA which accounts for 98.5% of the domestic US market and approximately 20% of the global market for pistachios.[6]

Arguably the majority of investment in thermochemical processing has been in the development of pyrolysis systems involving the thermal decomposition of biomass in the absence of oxygen to produce biochar, gas, and a liquid bio-oil, which may be further refined and blended with conventional liquid transport fuels for direct use.[7] Generally, there are considered to be three types of pyrolysis of biomass; Flash, fast and slow. In slow pyrolysis, the biomass is slowly heated at a temperature of up to approximately 400 °C, typically yielding a high proportion of biochar and smaller proportions of gaseous and liquid fuel fractions. In fast pyrolysis, the temperatures are typically above 500 °C with higher proportions of liquid pyrolysis oil being obtained and higher proportions of fuel gases being produced.[8] Ordinarily, pyrolysis oils contain a high proportion of oxygenates,[9] which have a deleterious effect on the stability of the fuel as well as cold temperature properties and energy density.[10] As a result, pyrolysis fuels require several further refining/treatment stages in order to increase their stability and make them suitable for use as a transport fuel.[11, 12]

Catalysed fast pyrolysis (CFP) has been researched increasingly over recent years, generally using zeolite catalysts. CFP aims to perform conventional fast pyrolysis, and simultaneously upgrade the resulting biomass derived gaseous species to more useful and valuable liquid fuel with a lower oxygen content to that of unrefined fast

pyrolysis bio-oil obtained without catalytic upgrading. The catalysts can be added to the reactor with the biomass to perform in-situ upgrading, or alternatively be used ex-situ, and catalyse the conversion of gaseous pyrolysis products.[13, 14]

Due to their low cost and ability to be handled easily, the most common catalysts employed for the upgrading of pyrolysis oils are zeolites. Zeolites are comprised of interconnected tetrahedrally arranged $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$. If each of the tetrahedra contain Si as the central atom, then the charge is balanced, however if Aluminium central atom is introduced, the zeolite takes on a negative charge. The negative charge of the aluminium is balanced by a positively charged counter ion. Commonly this counter ion is H^+ giving the zeolite strong acidic characteristics, useful in many examples of acid catalysed reactions.[15-17] The strength of the acidic nature of zeolites can be altered by using different counter ions as well as through dealumination, with higher ratios of Si/Al giving reduced acidity.[15, 16]

The strength of zeolites as catalysts lies in their natural ability to be size and shape selective with respect to the reactant that is able to be accepted into the porous structure, and the products that are able to be formed. This size and shape selectivity makes them ideal for production of fuels, where hydrodynamic volume of molecules is of such importance, indirectly affecting many of the requisite physical property parameters set out in specifications.[18, 19]

It has been reported previously that to be selective for biomass molecule upgrading rather than hydrocarbon cracking, a high Si/Al ratio is preferable. Bond energies of C-O are lower than those of C-C and as such require a less acidic zeolite to catalyse the bond cleavage and production of a smaller molecule. It was reported by Foster et al. that a Si/Al ratio of around 15 increases selectivity for C-O cleavage and for petroleum refining operations, a Si/Al ratio of 5-8 is more effective.[20]

Zeolites are most widely and perhaps most significantly used in the production of petroleum fuels,[21] for fluid catalytic cracking (FCC). FCC is used for production of around 45% of global gasoline supply, and involves the ‘cracking’ of larger hydrocarbons to smaller and branched chain hydrocarbons.[17] Zeolites have been investigated for deoxygenation of oxygen containing compounds, most notably the methanol to hydrocarbon (MTH) process, pioneered by Mobil in 1986, whereby methanol is produced from synthesis gas and then passed over ZSM-5 zeolites to convert them to short chain alkenes and high octane gasoline.[22]

Alternatively to CFP, several reports have suggested that catalytic slow pyrolysis can be achieved in a liquid phase rather than the vapour phase. This reduces the temperature requirement of the system while producing a more suitable fuel product, this reaction is termed Liquid Phase Pyrolysis (LPP).[23] Though only a handful of reports have detailed the use of this type of system.

This system uses refined petroleum 'carrier' oil with a minimum vaporisation temperature of 280 °C. The role of this carrier oil is to act as a heat carrier and aid in mass transfer. Reaction temperatures and residence times are within the slow pyrolysis range, between 250-300 °C. Depolymerisation of the biomass is catalysed by a zeolite, and a calcium hydroxide neutraliser has been reported to regulate acidity. The process is carried out at ambient pressure with the more volatile products, being continuously distilled out of the reaction vessel before being condensed and collected. While the few reports available report high yields of mainly hydrocarbon product, it is unclear how much of the cracked carrier oil adds to the final product and how much is derived from biomass.

4.2 AIMS

The aim of this chapter is to assess the LPP process for producing a suitable hydrocarbon fuel from pistachio hulls provided by the Wonderful Company. The process will be scaled to 1L stirred tank reactor, and primarily the proprietary zeolite 4Å will be investigated (termed the 'AlphaKat' zeolite). In the second half of the chapter a range of different zeolites will be screened for their suitability in producing a suitable biofuel blend.

4.3 Results & Discussion

A low temperature, biomass depolymerisation reaction, utilizing a zeolite 4Å was run in a petroleum oil heat carrier in a 1L 316 stainless steel mechanically stirred reactor. Initially the heating profile used, mimicked those used on the pilot plant with a ramp rate of 4.17 °C s^{-1} from room temperature to 150 °C, where it was held for 1 hour, with the intention of driving water from the catalyst and biomass. After one hour the temperature was ramped to 250 °C at the same rate where the reaction took place. During this time, distillate was collected in two locations. The first collection pot was located at the end of a water cooled condenser (set to 5 °C), and the second was collected in a collection vessel cooled with dry ice (-78 °C) set just before the exhaust. The process remained at ambient pressure throughout (Figure 4.3-1).

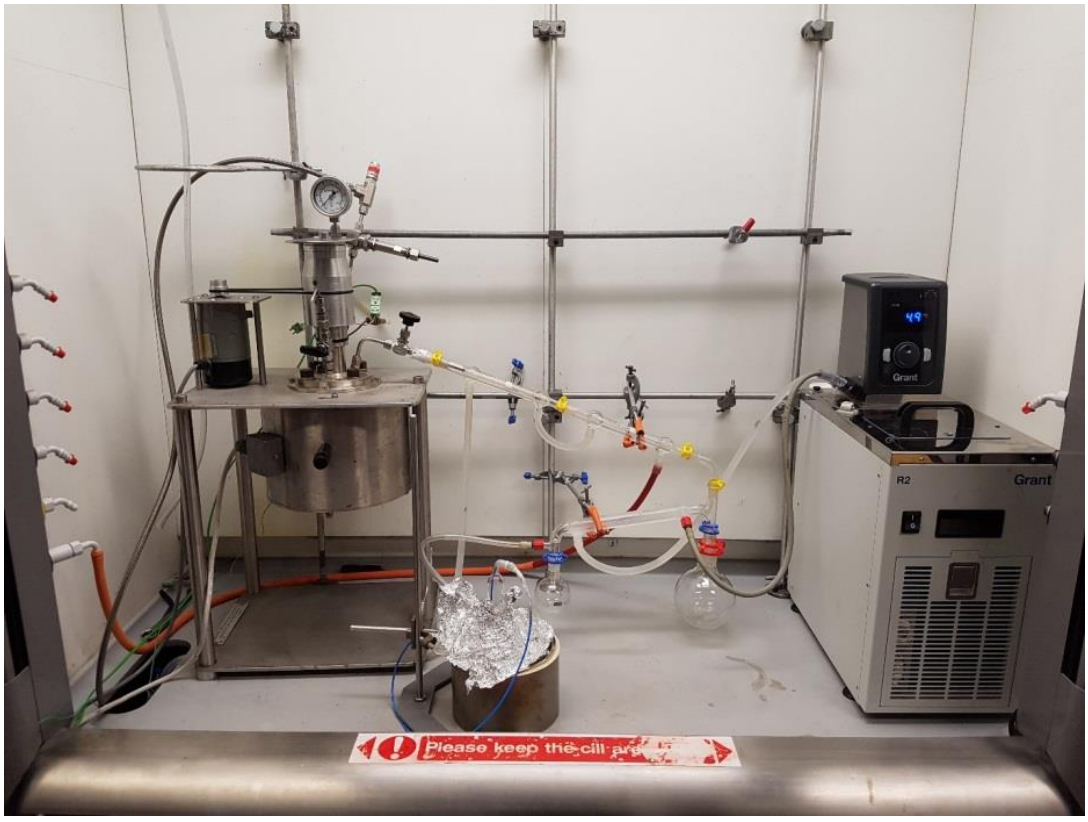


Figure 4.3-1: Photograph of reactor setup. Stirred reactor with 2 condensers run at ambient temperature, and 5 °C.

4.3.1 Carrier oil cracking

Zeolite catalysts are commonly used for the upgrading of heavy hydrocarbons to transport fuel range hydrocarbons. It is reasonable to assume that whilst the catalyst investigated, AlphaKat a type of zeolite 4A, may be active for the upgrading of biomass derived species, it will also retain the ability for cracking larger fossil oil derived hydrocarbons, such as the carrier oil used in this investigation.

The Alphakat zeolite was characterised as being Linde type A zeolites (Na:Al:Si = 1:1:1) Moisture content was determined to be 20-22 wt.%.

The extent to which the carrier oil was being cracked by the zeolite catalyst in the absence of biomass was determined, with the system run using just carrier oil (100g) with calcium hydroxide neutralizer and AlphatKat loadings of 2 wt. % and 20 wt. % with respect to the carrier oil.

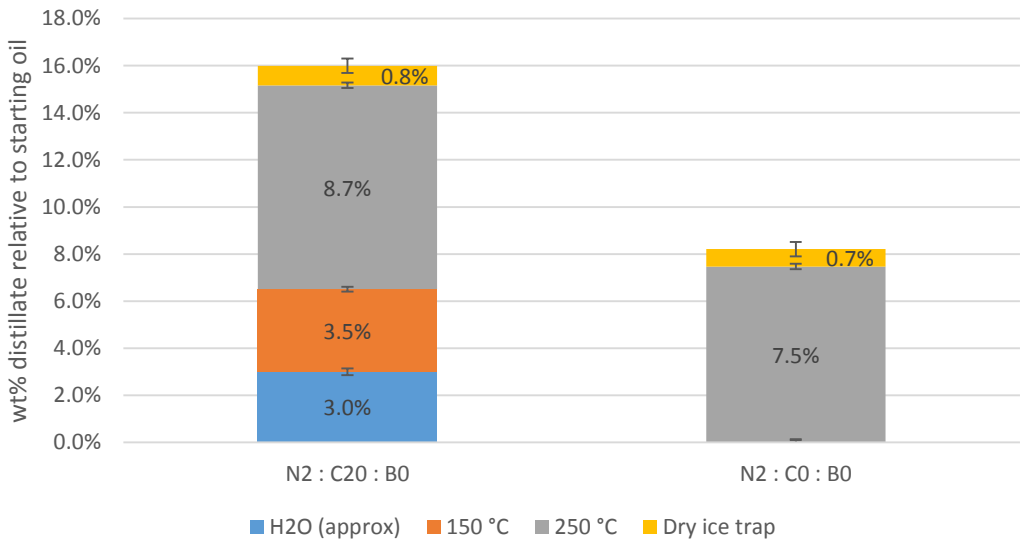


Figure 4.3-2: Weight % composition of distillate obtained from biomass free reactions, with and without catalyst, where N = neutraliser, C = catalyst and B = biomass. The error bars denote 1 standard deviation (n=3).

Distillate was obtained from the system at 250 °C, with water being driven from the catalyst after the reactor temperature reached 150°C. This resulted in a water content of the total distillate obtained from the system of approximately 3 wt% relative to the starting carrier oil. Whilst a water fraction is not a desirable in the obtained product, it is not problematic to separate from the hydrocarbon fraction through further

processing. It is unclear at this stage whether the water is due solely to the inherent moisture content in the biomass or catalysts or suggests that deoxygenation is occurring. The additional neutraliser was added in order to further react with any acidic species and thus reduce selectivity for C-C rather than C-O bond cleavage. A potential beneficial side effect is that it may stabilise the product bio-oil when biomass is used in the system. Upon investigation, it appeared that the $Ca(OH)_2$ neutraliser also acts as a co catalyst, with 7.5g of distillate being obtained in the presence of only neutraliser and no zeolite.

4.3.2 AlphaKat activity

As the AlphaKat zeolite was active in respect to cracking carrier oil, it is clear that product formed will not solely be a biofuel. To determine the effect of biomass on the system, pistachio hulls were pre-dried and ground down to <3mm pieces. 20g of this biomass was then added to the reactor. Promisingly distillate fractions were found to increase vastly on addition of biomass suggesting not only production of biofuel but also a further cracking effect on the carrier oil itself.

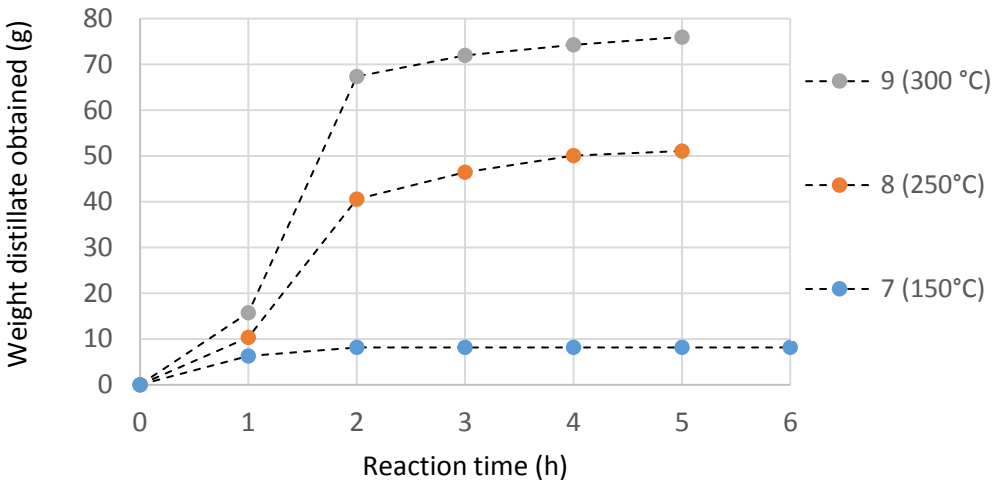


Figure 4.3-3: Distillate production profile of 3 reactions run at different temperatures.

The reaction was run at 3 temperatures, 150 °C, 250 °C and 300 °C. It was found that the water quantity in each reaction remained relatively constant, with approximately a 4-6g aqueous fraction being obtained each time. This is attributed to an approximately constant moisture content of the porous zeolite catalyst, and to a lesser extent the biomass.

Upon addition of 20g biomass to the reaction the quantity of distillate obtained rose significantly from 16.0 g to 51.1 g at 250 °C, a 35.1g increase. This suggests that the biomass itself acts to promote the cracking of the carrier oil, which could be as a result of an increase in acidity of the reaction mixture upon dissolution of the biomass and production, potentially with simultaneous production of biomass derived product. The catalytic effect of biomass ash is well documented in fast pyrolysis reactions, normally necessitating the continuous removal from the reactor.[24] It seems likely that a similar effect is observed in the LPP reaction.

There was very little distillate obtained at a reaction temperature of 150 °C (8.13 g) with approximately 50% of the distillate obtained being aqueous. At a reaction temperature of 300 °C a large increase in the quantity of distillate was observed, with 76 g being obtained, presumably due to an increase in the rate of catalytic activity, and also the distillation of the lightest portions of the carrier oil out of the reactor.

The catalytic activity of the Alphakat system is reduced dramatically after 2 hours. This could potentially be due to the lack of biomass left in the system or the production of coke, known to inhibit zeolite activity.[25] To determine the level of coke as well as the quantity of unreacted biomass, the solids were analysed by Thermogravimetric Analysis (TGA), figure 4.

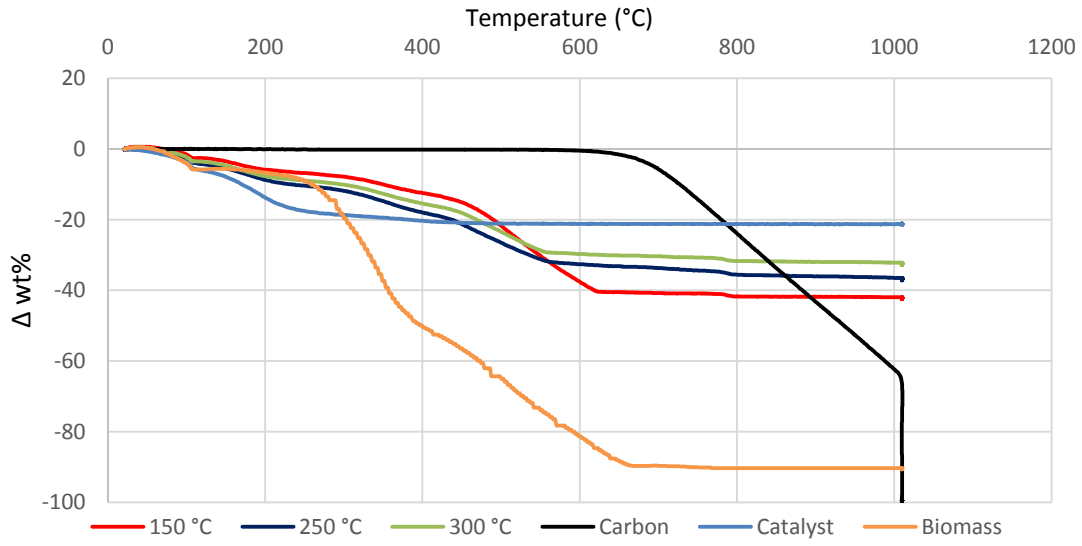


Figure 4.3-4: TGA traces of the reactions run at different temperatures, the starting biomass, fresh catalyst and a standard sample of carbon from Sigma Aldrich.

The Zeolite 4A showed a mass reduction of 21 % upon heating, with reduction starting shortly after the sample temperature reached 100 °C, indicating that water was being

released from the porous structure. There were no other losses observed after water had been driven off, and demonstrates that the majority of the water produced in the reaction comes from the catalyst.

In the case of the pistachio hull biomass, there are three distinct regions in the TGA trace. Firstly, up to 260 °C, water is being removed from the biomass (approximately 8 wt. %). Between 260 and 350 °C the hemicellulose in the husks is broken down, and between 350 and 600 °C, cellulose and lignin decompose. This analysis correlates well with previous studies carried out on the thermal decomposition characteristics of pistachio waste.[26] In total, 90.7 % of the biomass is lost, with the ash content of the biomass being approximately 9.3 %.

By subtracting the catalyst, ash and neutraliser left in the solids, as well as the water the TGA traces from the left over solids can be used to assess the level of biomass conversion.

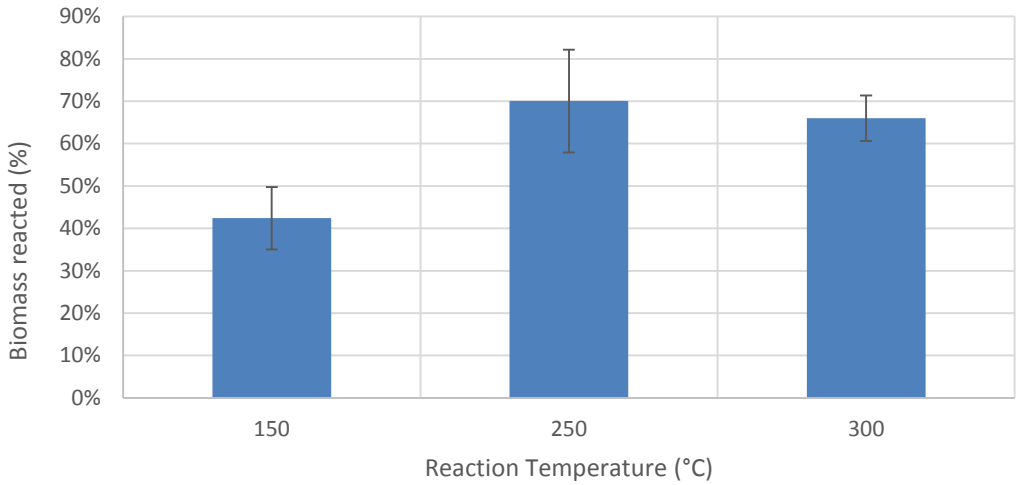


Figure 4.3-5: Estimated amount of biomass used in the reaction calculated from the TGA analysis of the solids at different temperatures

There is a positive correlation observed between reaction temperature and biomass conversion (Figure 4.3-5), with 55.6 % of non-ash biomass being utilised at 300 °C, dropping to 45.7 % and 33.3 % at 250 °C and 150 °C respectively. It appears that an increase in temperature is an efficient way to increase conversion of biomass.

There is strong evidence of coking, with up to 3.22 wt% (relative to catalyst) being observed in the reactions (Figure 4.3-6). It seems clear that the AlphaKat zeolite is being deactivated in the LPP rather than a reduction in activity being solely due to the lack of biomass feedstock.

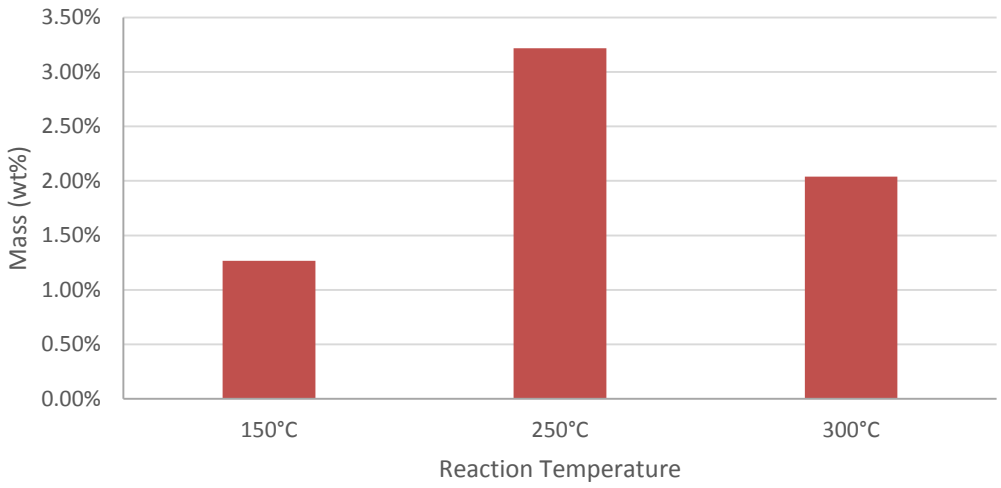


Figure 4.3-6: Mass of coke, relative to catalyst, formed in reaction at varying temperatures, as determined by TGA analysis (650-1000 °C).

4.3.3 Biofuel content in distillate

While a significant amount of biomass has reacted it is unclear whether this has produced very low temperature condensing gases, or how much of the biomass has partitioned into the distillate fuel phase. As any biofuel fraction in the distillate will be indistinguishable from the carrier oil, it is extremely challenging to determine the blending level. However, as the biomass is modern and the carrier oil is fossil fuel derived then ^{14}C dating can be used to approximate the blend level. This method works by measuring the quantity of the radioactive ^{14}C isotope relative to the more abundant ^{12}C. ^{14}C is a cosmogenic isotope and is primarily formed in the earth's upper atmosphere. There is therefore a consistent quantity of the isotope present in atmospheric CO_2 which is used by plant life during photosynthesis. Whilst ^{14}C decays to the more stable ^{14}N at a constant rate (t ½ = 5730 years), whilst a plant is alive the ^{14}C content within the plant is replenished. Once a plant dies, carbon is no longer taken up from the atmosphere and so the quantity of ^{14}C begins to deplete. This gives a measurable point of difference for chemically similar molecules contained within a fuel sample, some of which are derived from a biological source that has stopped growing recently and some of which are from a fossil oil source derived from biomass that ceased to uptake carbon millions of years ago.

Using this radiocarbon dating method, it was possible to quantify the proportion of biologically derived carbon in our samples, which gives an accurate indication of the content of biofuel in the distillate product (on a molar basis). Samples were analysed for the reactions run at 250 °C and 300 °C. A sample from the reaction at 150 °C was

not run due to the high cost of ^{14}C analysis and the apparent low efficiency of the reaction, making it unsuitable for further investigation.

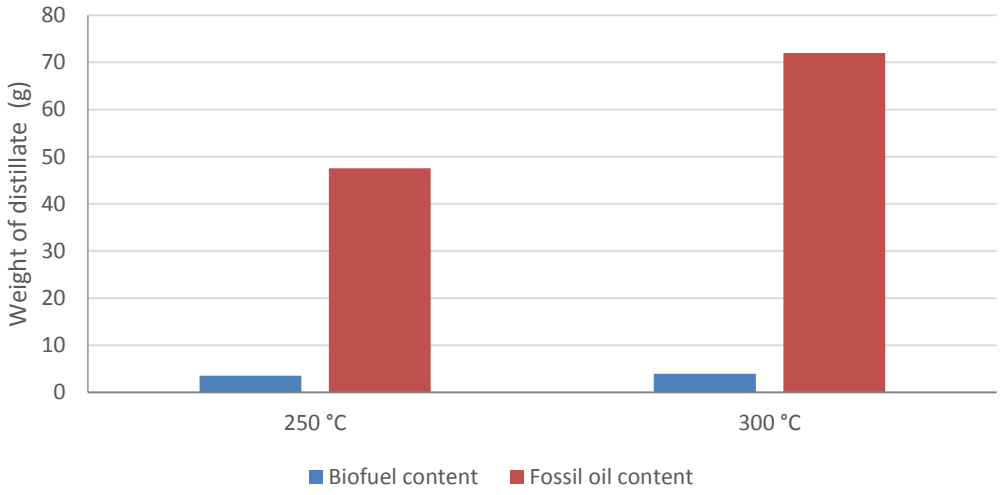


Figure 4.3-7: Estimated biofuel content of distillate product as determined by ^{14}C analysis.

It is evident that an increase in reaction temperature from 250 to 300 °C increases the absolute quantity of biofuel in the distillate mixture (Figure 4.3-7). However, whilst there is an increase in absolute terms, relative to the overall quantity of distillate, biofuel content, as determined by ^{14}C analysis, is less at 300 °C (5.1 mol %) than at 250 °C (6.9 mol %). Assuming equal C/H ratios between modern carbon and carrier oil species, there is 3.33 g of biomass derived carbon containing species in the reaction product at 300 °C and 3.03 g in the product at 250 °C, with 72.03 g and 47.55 g total distillate, respectively.

Table 4.3-1: Estimated level of conversion of the biomass into the biofuel, assuming 75% of available biomass can be converted, with a carbon content of 51 wt%.

Reaction temperature (°C)	Molar content modern carbon (%)	Modern carbon content weight (g)	% of available biomass to biofuel	% carbon from biomass into biofuel
250	6.9	3.03	20.2%	39.6%
300	5.1	3.33	22.2%	43.5%

Despite relatively low biological content in the final fuel, a significant amount of the biomass carbon is being distributed to this fraction (Table 4.3-1). In addition the maximum blend levels of many biofuels are 5-20%, and the LPP reaction might be a method of producing these fuels ready blended, without the needed for further blending. However, this would rely on the molecular and fuel properties of the resulting distillates being suitable for use as a transportation fuel.

4.3.4 Distillate fuel properties

To determine the suitability of fuels, the distillates were first analysed by ^{1}H NMR. The products of reaction at 150 °C are significantly different to that of reactions run at 250 °C and 300 °C as the portion analysed was predominantly aqueous. It is evident that there are some oxygenated species within this aqueous fraction such as esters and a high proportion of unsaturates. There is some evidence of pyrrole, which, if present in the bulk fuel product, would need to be removed. Relative to other samples, as would be expected, there is a much lower hydrocarbon content in this predominantly aqueous sample.

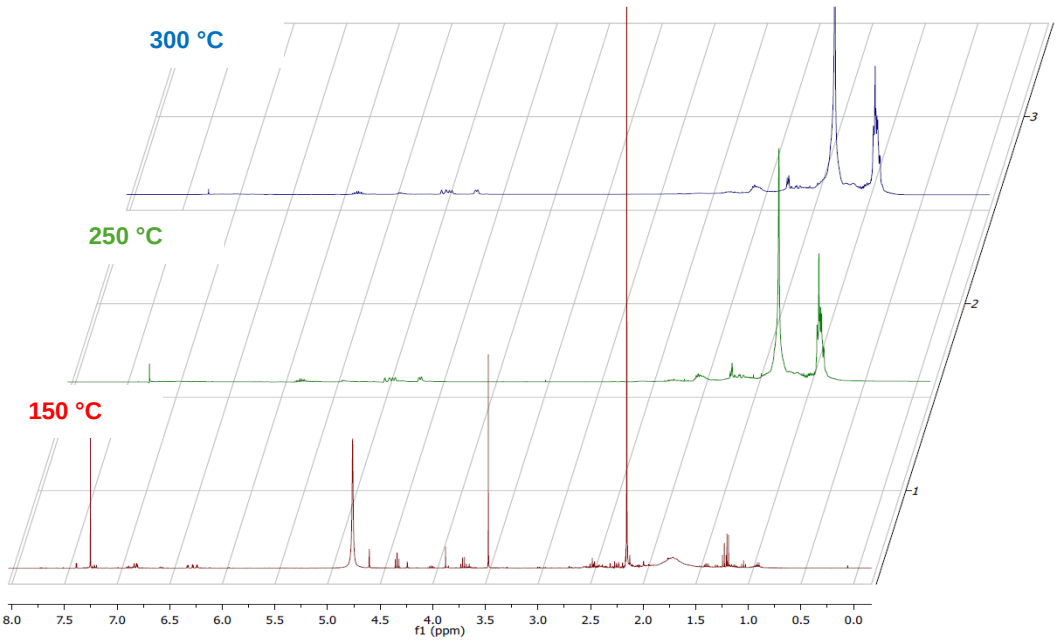


Figure 4.3-8: NMR spectra comparison if distillate products at 150, 250 and 300 °C.

At 250 °C and 300 °C, the products are nearly indistinguishable, with both product distillates consisting of high proportions of CH_2 and CH_3 moieties, and a small proportion of unsaturated hydrocarbons, typical of hydrocarbon cracking products. In all of the products, negligible quantities of aromatic compounds were detected.

The elemental analysis of the distillate from each of the reactions showed a higher C:H ratio in the product obtained from the 300 °C reaction relative to the same reaction at 250 °C. NMR analysis of the distillates showed chemically similar products, thus indicating a slightly longer chain hydrocarbon product from the reaction at 300 °C as would be expected due to increased vaporisation of higher boiling point species in the reaction mixture.

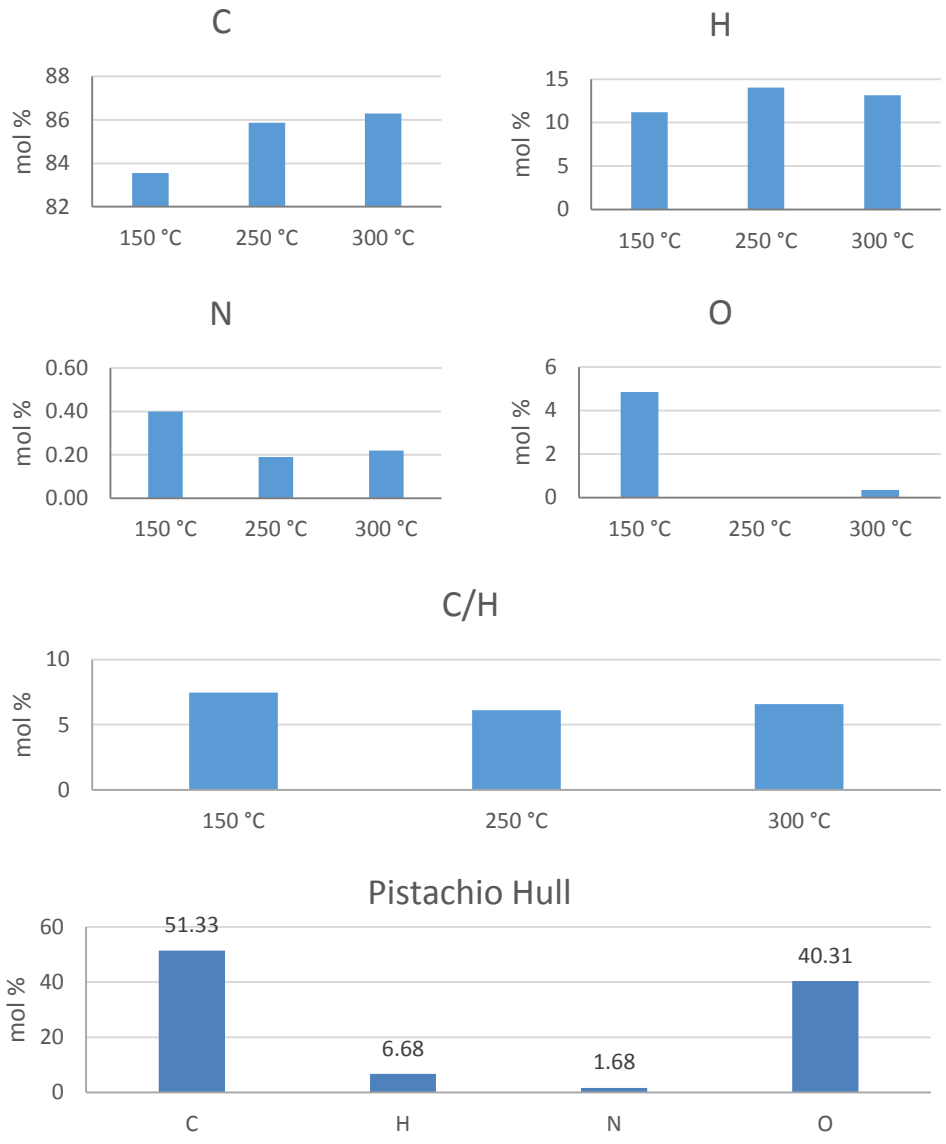


Figure 4.3-9: Elemental analysis of distillates obtained from reactions at 150, 250 and 300 °C and elemental analysis of the pistachio hull feedstock.

There is a notable lack of oxygenated species within the product mixtures with a maximum of 4.85% being observed in the 150 °C reaction product, compared with 40.31 % in the biomass feedstock (Figure 4.3-9). Ordinarily, pyrolysis based fuels would be expected to have a significantly higher oxygen content.

The lack of oxygen is in no small part due to the fact that of the distillate product, only 5-7 mol% is biofuel. Scaling the 0.35 % oxygen content of the 300 °C distillate to approximate oxygen content of the biofuel portion only produces a biofuel oxygen content of 8.85 mol%. For the reaction at 250 °C however, the fact remains that there is significant biomass loss, proven modern carbon content of 7% and negligible quantities oxygen within the fuel product. This leads us to believe that, unusually in the area of biomass to fuel conversion technologies, there is conversion of biomass to a high quality liquid hydrocarbon which has an exceptionally low and in some cases negligible oxygen content.

4.3.5 Continuous loading of biomass

In an attempt to increase the biofuel content in the fuels, a staged biomass delivery into the reactor was investigated. It was thought that with staged delivery, mass transfer may be improved. It is also necessary to determine the effect that different loading profiles have upon the reaction rate and efficiency, as when run on an industrial scale it is highly desirable to be able to run the reaction as a continuous or at least a semi-batch process for operational efficiency reasons.

The reaction conditions were identical to those used previously in the 250 °C reaction, however 20g of biomass was not loaded into the reactor at the start of the reaction, but instead 4 x 5g was added to the reactor from 1 hour through to 4 hours on an hourly basis. The quantity of distillate obtained was monitored from this point on.

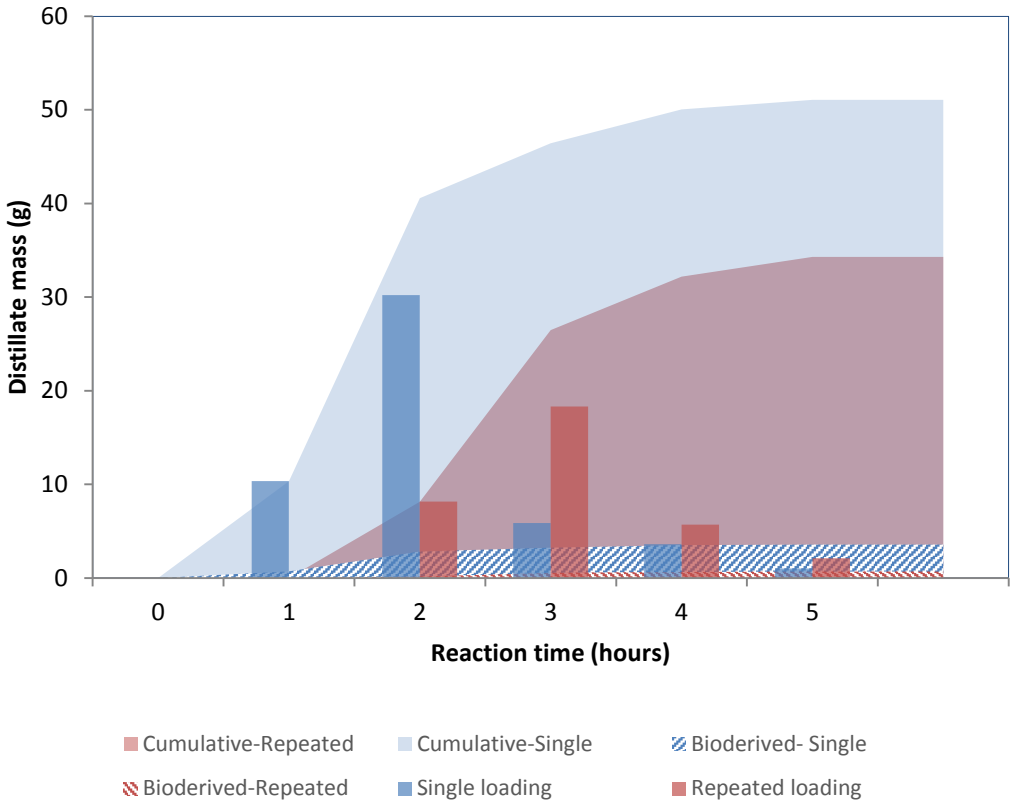


Figure 4.3-10: Distillate production each hour (bar), with total distillate (area) on one single loading (blue) and cumulative loading (red) of 5 g of biomass every hour

It is evident from comparing reactions with different loading profiles that the presence of biomass has a significant effect on the quantity of distillate that is obtained. In the case of a single loading of biomass, distillate is obtained much more quickly, with 10.34 g of distillate being present in the collection vessel after just one hour. With a repeated loading profile, where the first addition of 5g of biomass is not carried out until 1 hour of heating, there is no distillate collected in the collection vessel. Based on analyses earlier in the investigation which showed the majority of the distillate obtained is as a result of the zeolite catalyst cracking the carrier oil, so it would be expected that we would see very similar quantities of distillate obtained at each stage of the reaction for both loading profiles. However, this assumption relies on the fact that there is no synergistic/co-catalytic effect imparted by the presence of the biomass itself. A co-catalytic effect may be occurring as a result of an increase in acidity of the reaction.

Pyrolysis causes the degradation of hemicellulose and the formation of acidic species. The catalytic mechanism of action of zeolite 4A type catalysts relies on

reaction at acidic sites within the porous structure.[27] If the acidity of the bulk reaction mixture were to be raised, the acid catalysed cracking of carrier oil would be increased. It would be expected then that the presence of larger quantities of biomass within the reaction mixture would act to promote acid catalysed cracking of the carrier oil.

Table 4.3-2: Estimated level of conversion of the biomass into the biofuel, for the single addition and multiple additions, assuming 75% of available biomass can be converted, with a carbon content of 51 wt%.

Reaction type	**Molar content modern carbon (%)**	**Modern carbon content weight (g)**	**% of available biomass to biofuel**	**% carbon from biomass into biofuel**
Single addition	7.0	3.01	20.1%	39.3%
Multiple addition	2.0	0.55	3.7%	7.2%

Using this staged introduction of the biomass had a negative effect on the proportion of modern carbon present in the distillate product, with only 2 mol % of the distilled product consisting of biomass derived carbon, this equates to only 7.2% of the avialble carbon from the biomass going into the biofuel (Table 4.3-2). When compared with the 7 mol % obtained with a single loading of biomass at the beginning of the reaction, this is a significant reduction, and supports the assertion that there is a co-catalytic effect imparted by the presence of the biomass substrate.

4.3.6 Carrier oil reuse

Another possibility to increase the biofuel content is to reduce the input of carrier oil by reusing what is left in the reactor. It is possible that the reaction produces a heavy bio-oil, which is not distilled out of the system, this could potentially replace the carrier oil that is lost from the system due to being cracked and distilled. To investigate this effect, reactions were run reusing the carrier oil to determine the rate at which it is depleted, and to determine whether there is an accumulation of biomass derived species within the carrier oil after multiple uses (Figure 4.3-11).

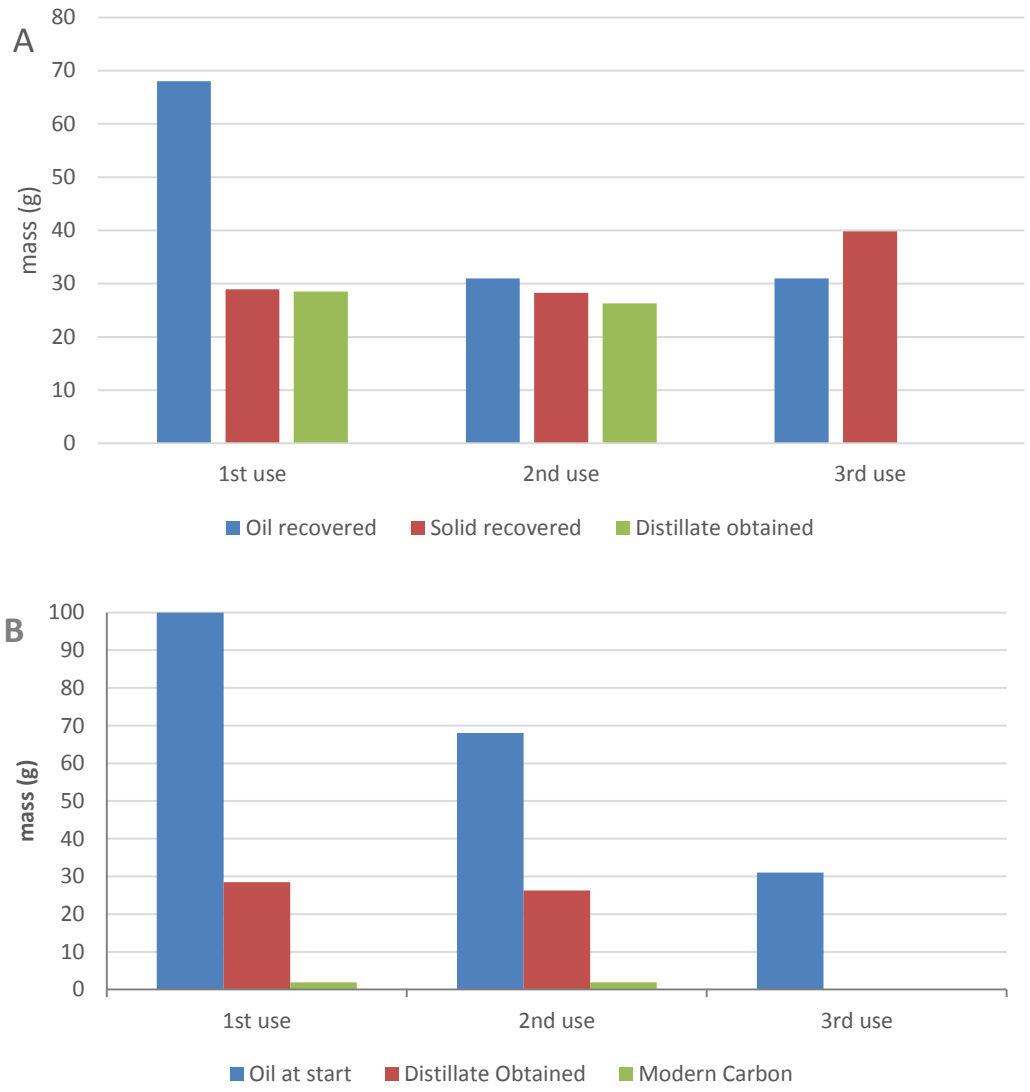


Figure 4.3-11: (A) Distillate production with corresponding carrier oil and solid depletion for carrier oil reuse reactions. (B) Oil left in the reactor vs the distillate recovered

The first use reaction showed a 65.5 % reduction in biomass, and 68g of carrier oil was left after the reaction. After reloading the reactor with fresh catalyst and biomass 68.8 % of the new available biomass was used. At this point only 31 g of oil was left in the reactor. On the third use the carrier oil had depleted to an extent, where the introduction of new catalyst and biomass to the oil caused the formation of a paste, rather than a suspension that is able to be stirred. No distillate was observed, and it seems that the mass and heat transfer had been reduced to an extent where effectively no reaction was seen. Interestingly, there was very little reduction observed between first and second reactions, suggesting that the reaction is not limited by the availability of substrate in the reaction mixture. The lack of any appreciable depletion in the quantity of distillate obtained also indicates that any heat and mass transfer

change due to this higher solid to carrier oil loading ratio does not negatively impact on the reaction efficiency.

In each instance the depletion in carrier oil matches well with the amount of distillate obtained from the reaction, indicating that, in line with previous experiments, much of the product is derived from the carrier oil itself. Radiocarbon analysis revealed that selectivity for biomass species remained constant, with distillate products containing 7 mol% modern carbon for distillates from both the 1st and 2nd reactions (Table 4.3-3).

Table 4.3-3: Estimated level of conversion of the biomass into the biofuel, for the reactions reusing the carrier oil, assuming 75% of available biomass can be converted, with a carbon content of 51 wt%.

Reaction type	**Molar content modern carbon (%)**	**Modern carbon content weight (g)**	**% of available biomass to biofuel**	**% carbon from biomass into biofuel**
First use	7.0	1.71	11.4%	22.4%
Second use	7.0	1.58	10.6%	20.7%

NMR analysis suggests that there is little accumulation of biomass-derived species in the remaining carrier oil (Figure 4.3-12: NMR spectra of remaining oil after each use of carrier oil reuse runs. Lack of difference would indicate no bio-derived species accumulation. In combination with a trend of carrier oil depletion across repeated reactions, the results would suggest that carrier oil is not replaced.

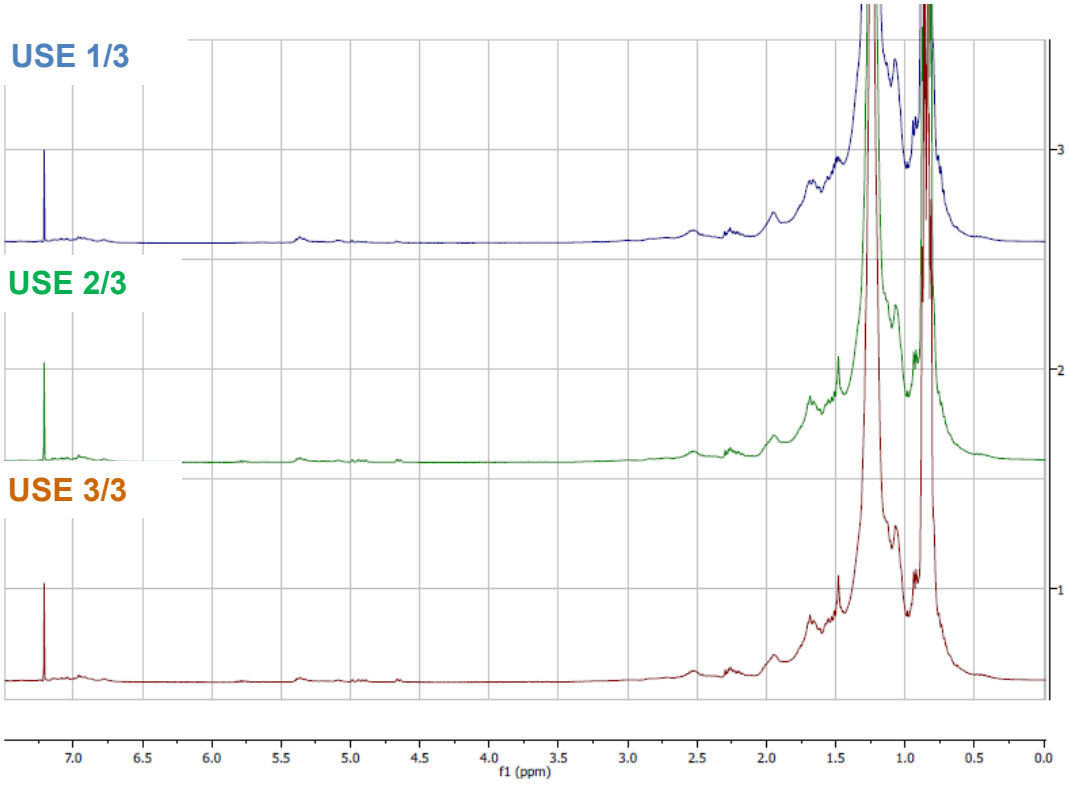


Figure 4.3-12: NMR spectra of remaining oil after each use of carrier oil reuse runs. Lack of difference would indicate no bio-derived species accumulation.

As carrier oil is not replaced, it is probable that the quantity of carrier oil would need to be augmented through further addition of new carrier oil, throughout a continuous process, or alternatively in between reactions in a batch process. This requirement would likely add significantly to the cost of running the process and it is suggested that the addition of approximately 30 wt.% of the carrier oil on a regular basis, would likely render the process economically unviable, and would impact negatively on the environmental sustainability credentials of any fuel produced using this technology. It would seem then, that the system works for the production of a potentially excellent fuel, however its excellence is largely due to the fact that 93-95 wt.% of the distillate obtained is actually derived from the carrier oil- itself a high quality petroleum product.

It seems that whilst this process does present a way of converting pistachio hulls to biofuel, zeolite 4A is not selective enough for biomass derived molecules, exhibiting a propensity to crack the carrier oil to a greater extent than upgrading the biomass-derived species within the reaction mixture. This results in an inefficient, and ultimately unacceptable yield of biomass derived fuel, relative to cracked carrier oil product.

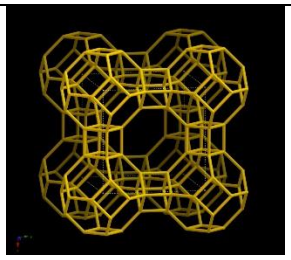
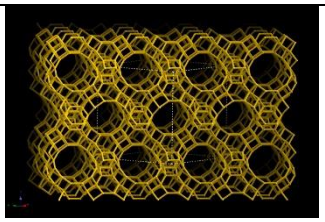
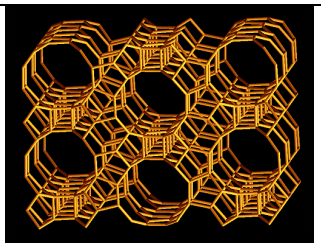
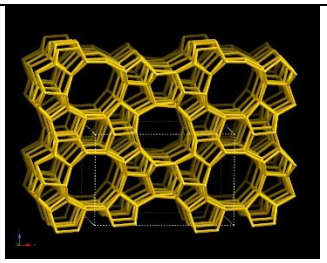
In order to address this issue, after consultation with partners at California Institute of Technology it was decided that other, potentially more suitable catalysts would be screened for activity and particularly specificity for the upgrading of biomass-derived species.

4.4 Catalyst Screen

Five alternative Zeolite catalysts were investigated for suitability in the LPP system. The first was H-USY, this is a more stable counterpart to Y zeolite, and is prepared through the steaming of that zeolite. This imparts not only extra framework characteristics such as an important mesoporous structure but also a high thermal stability making it particularly suitable for industrial applications.[28] The presence of mesoporous structure within the zeolite has shown to increase the proportion of liquid rather than gaseous products when used in petroleum fuel refining.[29]

H-Beta zeolite was also screened, the Beta framework consists of 4, 5, 6 and 12 membered rings. It has previously been reported to be selective towards production of a diesel range product rather than a gasoline/naphtha range as afforded by zeolite 4A type catalysts.[30] The same zeolite was also used with an NH_4 counter ion. This undergoes ion exchange more easily than its protonic equivalent, and causes less acidification of the reaction mixture, potentially reducing the amount of carrier oil that is cracked. These catalysts were compared to Mordenite Framework Inverted (MFI) structured zeolites, also known as ZSM-5. This catalyst is commonly used in the petroleum industry to catalyse cracking and isomerisation of hydrocarbons. The protonic form of this zeolite provides the most acidic zeolite and was screened as the H form and the NH_4 (Table 4.4-1).

Table 4.4-1: Key parameters of zeolite frameworks investigated. Figures sourced from Database of Zeolite Structures.[31]

Framework	Max diameter of diffusion channels	Accessible volume of framework	Pictorial Representation
LTA (Alphakat)	4.21 Å	21.4%	
USY	7.35 Å	27.42 %	
Beta	5.95 Å	20.52 %	
MFI	5.50 Å	9.81 %	

Reactions were run so as to determine the efficiency of the catalysts with respect to the selectivity for biomass-derived molecules relative to those of within the carrier oil, and also to determine the hardiness of the catalyst, and to what extent reuse affected catalytic activity. The catalysts were added to reactions in an analogous way to those using zeolite 4A. Reactions were run once with distillate collected and analysed. 20 g of new biomass and 100 g of new carrier oil were then added to the reaction vessel and the reaction run again, using the same catalyst for a second time (Figure 4.4-2).

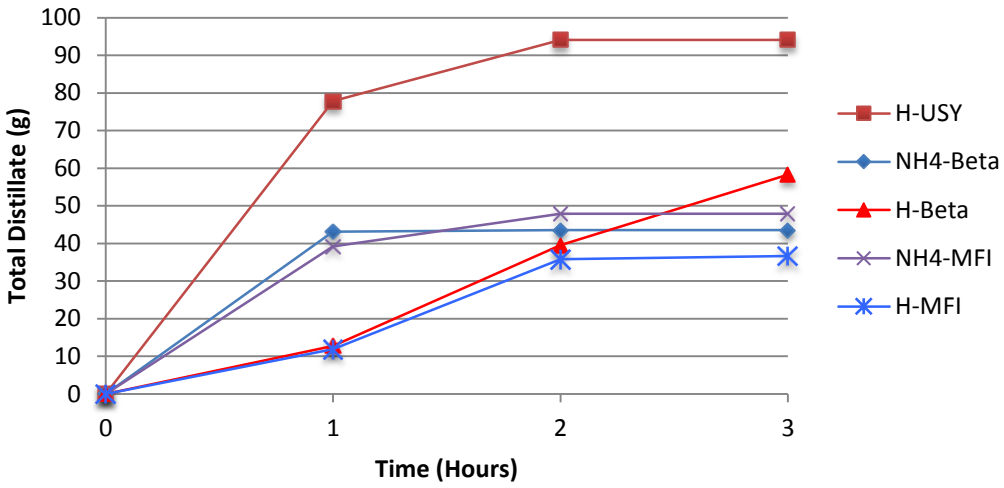


Figure 4.4-1: Cumulative mass of distillation products produced for the first use catalysts, H-USY, NH_4-Beta, H-Beta, NH_4-MFI and H-MFI

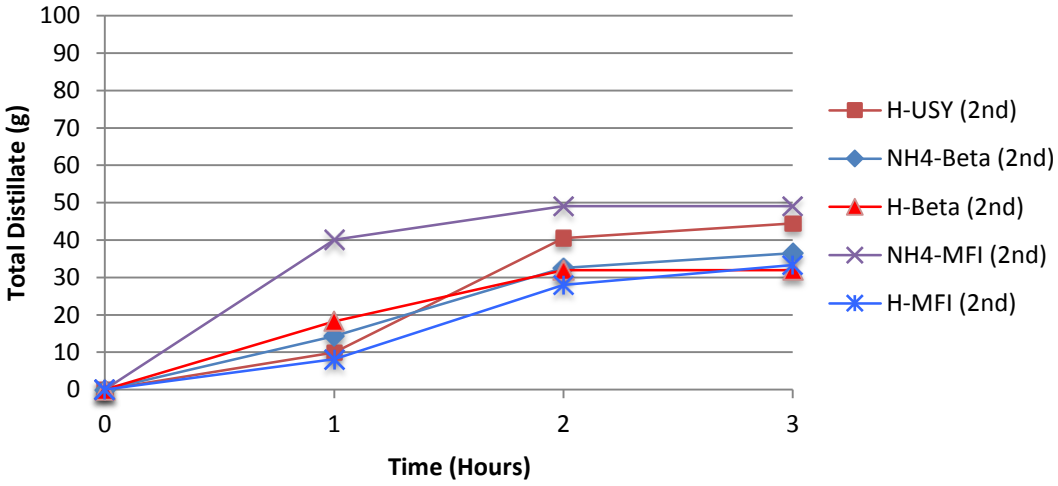


Figure 4.4-2: Cumulative mass of distillation products produced on 2nd reuse for the catalysts, H-USY, NH_4-Beta, H-Beta, NH_4-MFI and H-MFI

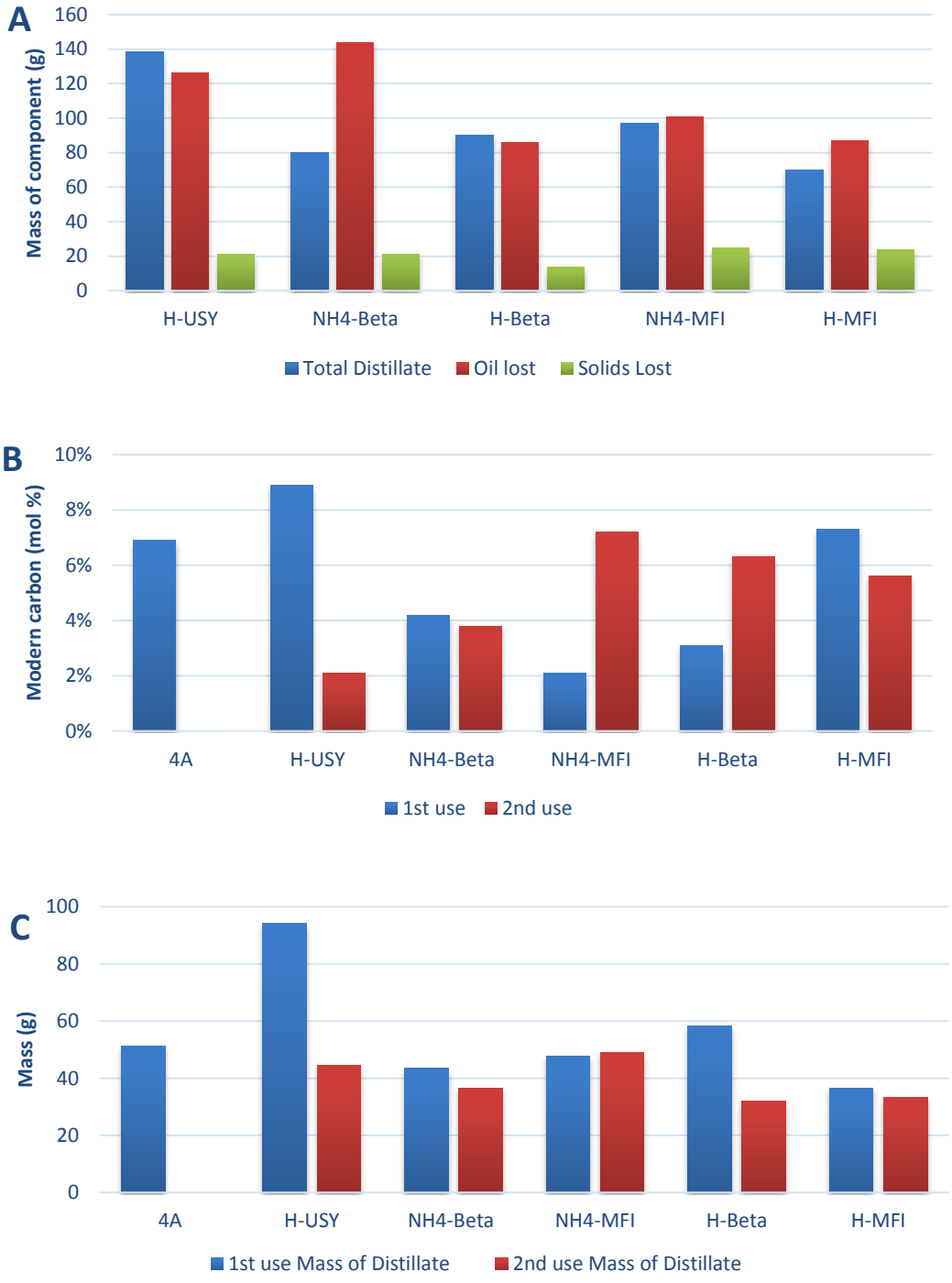


Figure 4.4-3: (A) mass changes of reaction components after 1st and 2nd catalyst use reactions. (B) Modern carbon content of distillate products from catalyst 1st and 2nd uses. (C) Mass of distillate obtained from 1st and 2nd catalyst uses.

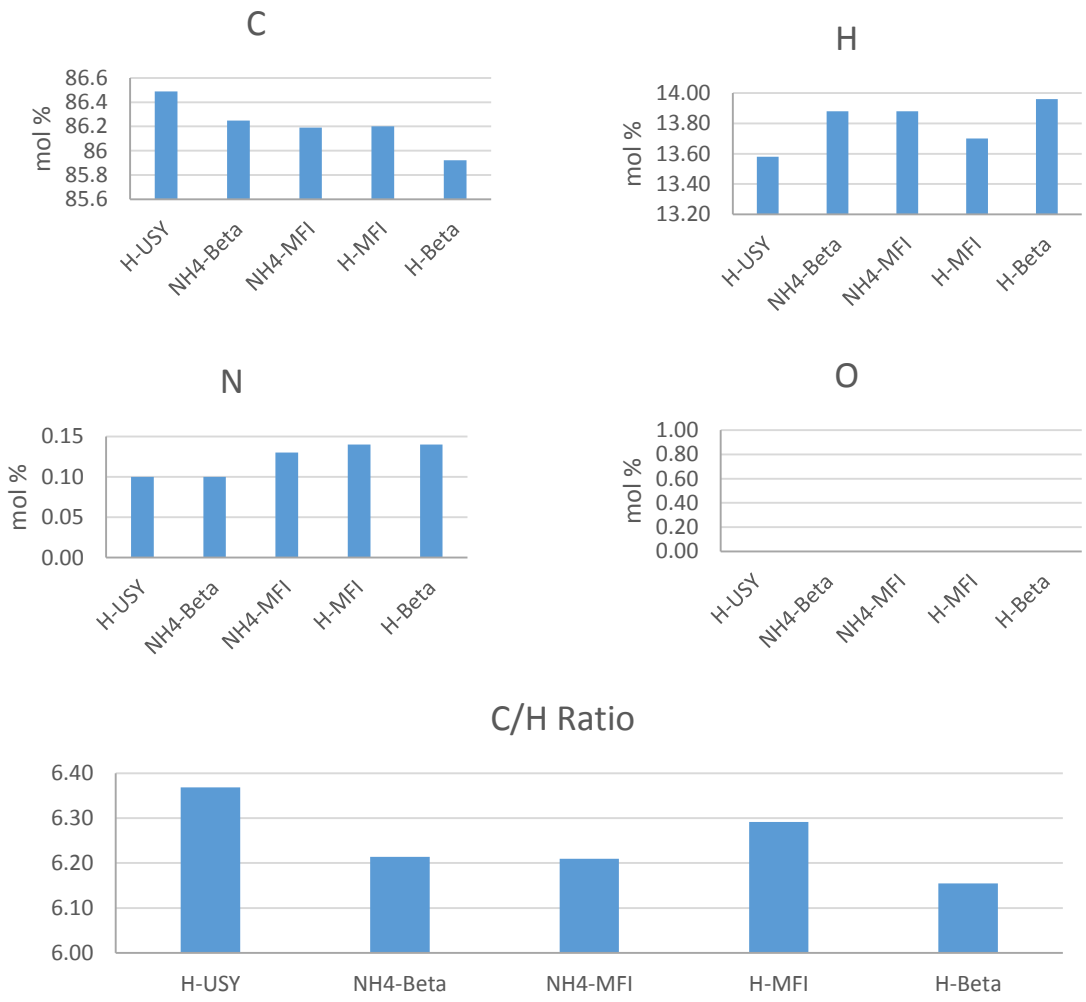


Figure 4.4-4: Elemental analysis showing of distillates obtained when using alternative catalysts.

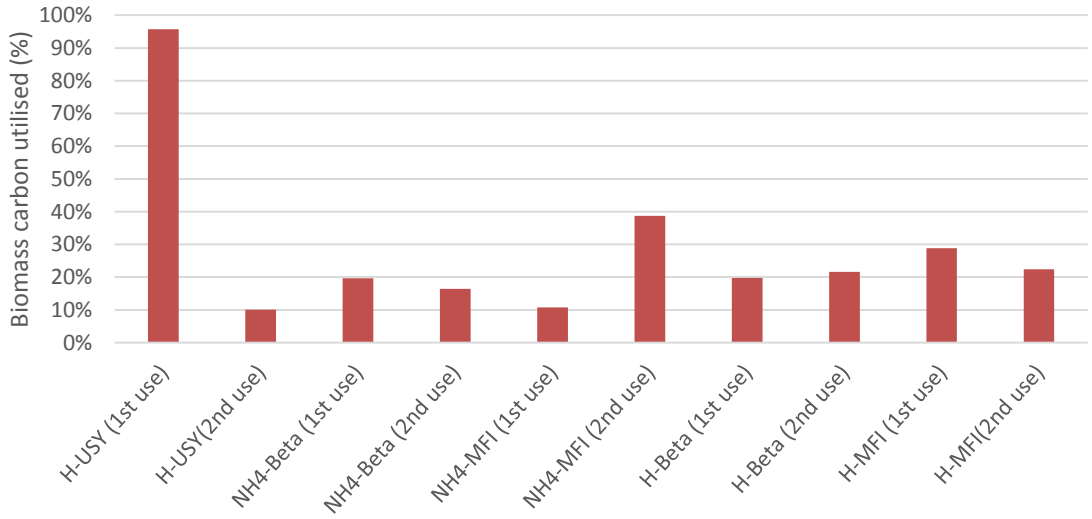


Figure 4.4-5: Proportion of available biomass derived carbon present in distillate product. Available biomass carbon calculated by combination of TGA and elemental analysis data.

4.4.1 H-USY zeolite

H-USY has been investigated previously for suitability in CFP systems, and found to be a very efficient catalyst for the conversion of alkaline lignin, showing a propensity for formation of higher quantities of aromatics when compared with other alternative zeolite frameworks.[30] This is attributed to the comparatively large micropores which also are reported to significantly reduce susceptibility to coke formation and subsequent deactivation.[31]

In this investigation, H-USY showed a high activity upon first use, with 94g of liquid distillate being obtained (Figure 4.4-2). The large volume of distillate (relative to other experiments) is indicative of not only a high activity, but also that the zeolite has a pore structure which promotes conversion of substrates to products with a condensation temperature above room temperature, rather than gaseous products which do not add to the liquid fuel distillate. The production of a liquid rather than gaseous fuel is highly desirable in the context of this technology and biofuel production.

Upon reuse, H-USY exhibits the largest reduction in activity of all the alternative catalysts screened, generating only 44.5 g of liquid distillate; a drop of 53 % (Figure 4.4-3). In addition, the initial rate of catalysis also appears much slowed relative to the first use. Whilst the initial rate is slowed upon reuse, activity is not completely absent, and between one and two hours the rate increases before reducing in the last hour of reaction. Potentially there is poisoning of the Brønsted acid sites occurring due to Na^+ ions present within the biomass.[31] Another potential mode of deactivation is the obstruction the porous structure by solids, such as coke formed during the first reaction. Commonly these types of zeolites are highly susceptible to coke deactivation that causes the total catalytic effect to be reduced.[30] The relative delay before reactivation of the catalyst occurs in the 2nd reaction when compared to the first, could however be due to obstruction of the pore structure by compounds that are soluble only at higher temperatures, and during the temperature ramp phase, do not initially allow access to the acidic catalytic sites within the zeolite.

Total liquid distillate obtained over both reactions for H-USY was 138.5 g, compared to a depletion of carrier oil of 126 g, substantially higher than the AlphaKat zeolite.

Depletion of solids over the course of both reactions was a total of 20.95 g, the second lowest biomass utilisation of the alternative catalysts tested, after the H-Beta catalysed reactions. Biofuel content of the distillate obtained, as determined by 14C

analysis was 9 % on first use and 2 % upon reuse of the catalyst (Figure 4.4-3). This shows a 2 % increase in the biofuel proportion of the obtained distillate when compared with zeolite 4A. The significant drop off in activity and particularly selectivity for biomass derived compounds is marked however. The resilience of the catalyst is an important factor both economically and logistically, and an effective one reaction lifetime is unlikely to be adequate for an industrial process.

4.4.2 BETA Zeolite Catalysts

The H-Beta catalyst showed an increased total distillate production compared with the AlphaKat, producing 58.3 g of distillate on first use, compared with 47.6 g (Figure 4.4-2). However, the Biofuel content of the distillate was determined to be only 3 mol % on first use, with the catalyst showing a marked selectivity for cracking carrier oil rather than the biomass.

In contrast to H-USY, the profile of distillate production indicates higher activity at higher temperature with a faster rate of distillate production observed after one hour, rather than during the temperature ramp phase.

Reuse of this catalyst yielded 32.0 g of distillate constituting a 45.2 % reduction from first use (Figure 4.4-3). The production profile of the distillate obtained remained the same as with the first use, with distillate production occurring predominantly after the reactor had reached temperature after 1 hour. The mass of distillate obtained was higher than that of the carrier oil used in the reaction, suggesting little formation of gaseous products.

The use of NH_4^+ as a counter ion rather than H^+ reduces the acidity of the zeolite, and the reactivity with respect to acid catalysis. For the NH_4^+ zeolite 43.5g of distillate was obtained upon 1st use of the catalyst, with a reduction to 36.5 g upon reuse, constituting a 16 % reduction in activity. On first use, the majority of catalysis was observed within the first hour, however, when used for a second time the majority of distillate was obtained once the reaction was up to temperature, between 1 and 2 hours. This delay in activity may be due to obstruction of the pore structure by compounds soluble only at higher temperatures, limiting access to the catalytic sites within the zeolite.

The total mass of distillate obtained over both reactions was approximately 44g less than the mass of carrier oil originally used for reaction. Coupled with a total solids utilisation of 21.3 g, it is apparent that much of the carrier oil is cracked to gaseous

products when using this catalyst. The biofuel content of the produced distillate as determined by ^{14}C analysis was 4% on both first and second uses of the catalyst, lower than most other catalysts screened.

4.4.3 MFI catalysts

Between first and second uses, the distillation profile from each of the reactions with this catalyst were extremely similar, with only a slightly slower initiation being observed upon reuse when compared to fresh catalyst. Total distillate mass obtained reduced by only 2.6 % between uses with 87.1 g of distillate obtained from both reactions (Figure 4.4-2) with an associated loss of 24.0 g of solids, and 87.1 g of carrier oil. When combined with a biofuel content of 7 % on first use, and 6 % for second use of the catalyst, (Figure 4.4-3) it appears that there is some, but not significant conversion of carrier oil to a gaseous product, a desirable characteristic for the production of a liquid fuel.

Similarly to H-MFI, on using NH_4-MFI for this reaction, no significant reduction in catalytic activity was observed when reusing the catalyst (Figure 4.4-3). Total carrier oil converted into product distillate over the course of the two reactions was 101 g, more than the same catalyst with an H^+ counter ion. 97.0 g of distillate was obtained from the reactions, with a depletion of 24.7 g of solids, suggesting that only a small portion of the carrier oil is being cracked to gaseous products, proportionally less gas is produced than in the case of H-MFI.

From ^{14}C analysis, biofuel content of the distillate was found to be only 2 % on first use, rising to 7 % on reuse. It is unclear why the selectivity increased so dramatically though it is possible that a change in acidity between the two uses could be a contributory factor.

Qualitative characterisation of each of the distillate products was also carried out using ^{1}H NMR spectroscopy (Figure 4.4-6).

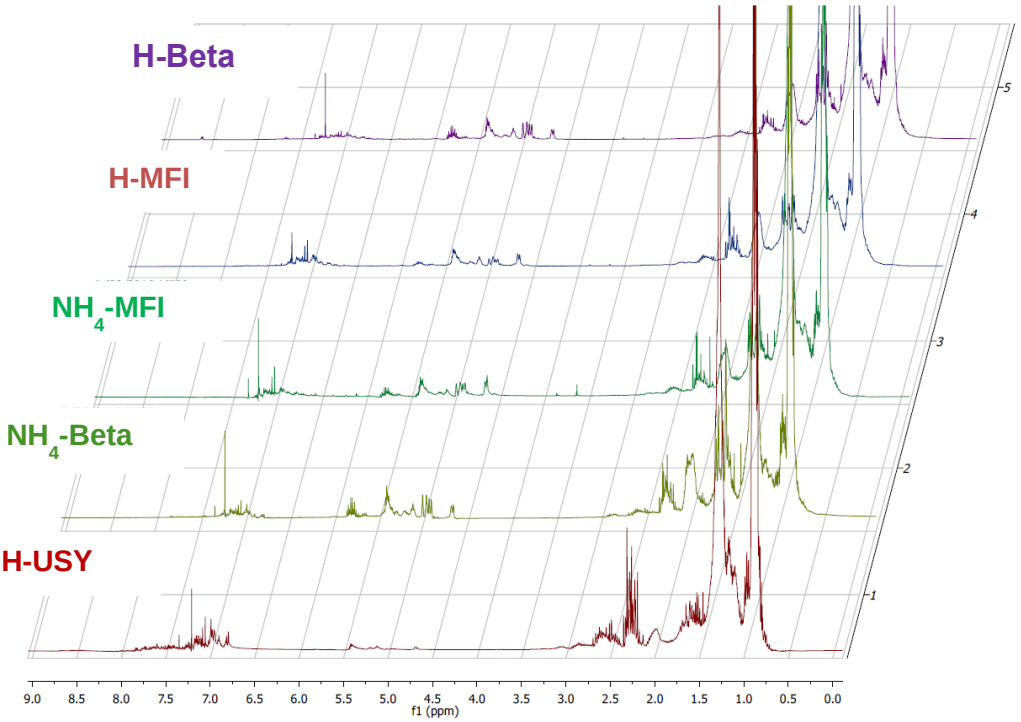


Figure 4.4-6: ^{1}H NMR analysis of distillate products produced using alternative catalysts

Depending on the structure of the zeolite and the counter ion used, resultant distillate quantities differed. For all of the alternative catalysts investigated, conversion of carrier oil was observed, with no catalyst showing a significant bias toward conversion of biomass-derived species with all distillate products containing between 2 and 9 mol. % modern carbon, compared with 7 mol % afforded by use of the conventional AlphaKat zeolite. H-USY gave the most notable combination of efficiency and alternative selectivity, with a large quantity of distillate product being produced on first use. This agrees with observations from CFP investigations conducted previously.[13] A relatively low proportion of unsaturated products and a higher proportion of aromatics was observed in the distillate product mix compared with other catalysts screened. This is attributed to the relatively large pore size of the USY framework allowing for larger molecules to access acid sites within the catalyst. Whilst higher aromatic content may lead to higher particulate emissions when used as a fuel, it would also impart desirable characteristics to the fuel, such as 'seal swelling' preventing leaks within fuel systems.[33] A lower proportion of unsaturated bonds within the product would also be likely to increase the fuels stability, conventionally one of the biggest hurdles in utilisation of pyrolysis oils as transport fuels.

Other than in the case of H-USY, all of the catalysts produced a qualitatively similar product, making the points of difference for consideration the proportions of biofuel

content within the respective distillate products, the absolute quantity of distillate obtained and catalyst reusability.

4.5 FUEL PROPERTIES TESTING

Fuel properties analysis is a vital part of alternative fuels development. Properties specified in documents from various regulatory authorities, such as ASTM D975 for diesel fuels or DefStan 91-91 for Aviation kerosene, are included for different reasons. Some properties such as the flash point temperature are included for safety reasons, whereas some properties, such as the kinematic viscosity, are included to avoid issues with fuel flow and pump wear. Other properties, such as the distillation profiles, are simply descriptive of the conventional fuels, and as such are not as important to try and mimic when developing a totally novel fuel; at least from an operational point of view. To assess the various fuels produced in this chapter some of the main fuel properties, namely the kinematic viscosity, energy content, freezing point and flash point were examined for the fuels obtained from the first distillate.

4.5.1 Kinematic Viscosity

The kinematic viscosity of the distillate products from each of the reactions was determined in accordance with ASTM D445 (Figure 4.5-1).

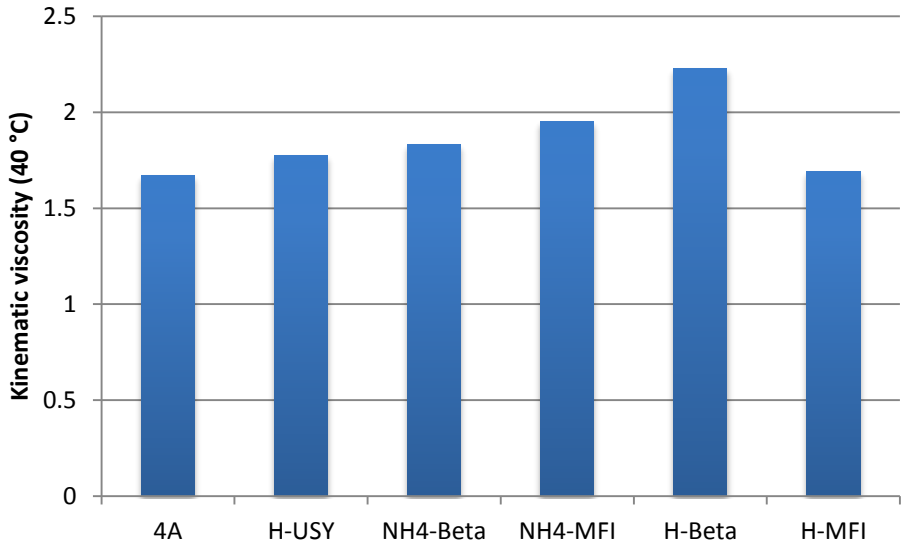


Figure 4.5-1: Kinematic viscosities of distillate product for each of the zeolite catalysts

Viscosities at 40°C were found to range from 1.67 to 2.23 $mm^2 s^{-1}$. Within this range, with respect to this criterion all the fuels produced by the six catalysts investigated would be acceptable as a replacement for diesel fuel. In order to ascertain suitability as an aviation fuel, the kinematic viscosity were tested at -20 °C. However, presumably due to the longer chain straight alkanes produced, none of the fuels would be suitable as an aviation jet fuel as all the fuels tested had a kinematic viscosity above 25 $mm^2 s^{-1}$ and as such would not satisfy the specification maximum as set out in DEF-STAN 91-91 of 8$mm^2 s^{-1}$.

4.5.2 Freezing Point Temperature

The temperature at which a fuel freezes is important for both operational and safety reasons. If a fuel solidifies it cannot be pumped, and as a result cannot be transported to the engine. Another possibility is that a small portion of the fuel starts to freeze and fuel filter blockages occur. This phenomenon would cause fuel starvation of the engine and cause the engine to stall, or flame out in the case of a gas turbine.

The freezing point temperatures of each of the samples were determined using a low temperature freezer. Freezing points were found to be between -22 °C and -33 °C, with the original AlphaKat catalyst, producing a product with a melting point temperature of -32 °C.

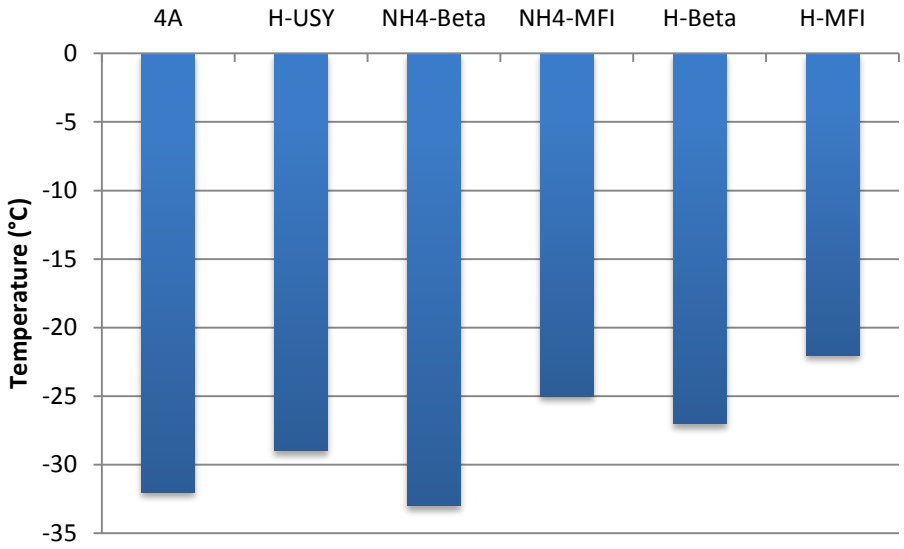


Figure 4.5-2: Freezing point temperatures of distillate products from each of the zeolite catalysts.

The fuel produced using H-MFI as the catalyst possessed a higher melting point product mixture than any of the other catalysts tested, -22 °C (Figure 4.5-2). This

tendency toward higher melting point products is shared with the structurally similar NH_4^+-MFI, suggesting that the pore structure of these zeolite frameworks is selective towards longer chain products than the products obtained when using the other catalysts examined. The lowest temperature melting point of -33 °C was exhibited by the distillate of the reaction using NH_4^+-Beta. The structurally similar H-Beta, exhibited a melting point of -27 °C. H-USY produced a product distillate with a melting point temperature of -29 °C.

In order to meet the specification freezing/melting point temperature criteria as set out in US and European specifications (ASTM D975 & EN590) the cloud point, or point at which frozen particles start to appear within the fuel, must be between +5 °C and -32 °C depending on the location in which they are being used. With respect to this criterion, all the fuels produced would satisfy the specification requirements for use as a diesel fuel. To be used as a replacement aviation kerosene the freezing point temperature must be somewhat lower with a specification maximum of -47 °C. All of the fuels produced here fail to meet that requirement, and as such, either blending with a lower freezing component, or further processing would be required for use as an alternative aviation kerosene.

4.5.3 Energy Density

One of the most important operational and economic considerations in production of a liquid transport fuel is its gravimetric energy density. This is the amount of energy that is released when a defined quantity of fuel is combusted.

Energy density is a particularly important parameter when considering a fuel for use in the aviation industry due to limited fuel tank volumes dictating the range of an aircraft, and also limited 'maximum take-off weight' of each airframe limiting the total payload of an aircraft, meaning that if the aircraft is able to use a more energy dense fuel, more passengers/cargo can be transported.

The fuels produced in this investigation possess a high gravimetric energy density, ranging from 45.1 to 46.0 MJ/kg (Figure 4.5-3). Diesel fuel specifications do not state a lower limit for Energy content, however fossil oil-derived diesel generally exhibits a gravimetric energy density of 42-45 MJ/kg.[34] Jet A-1 specification for aviation kerosene requires a minimum gravimetric energy density of 42.8 MJ/kg.

It is suspected that the high energy density exhibited here is due largely to the 91-98 mol% portion of each fuel consisting of non-biomass derived hydrocarbons, and as

such bearing a large similarity to the petroleum fuels for which the specifications were originally written.

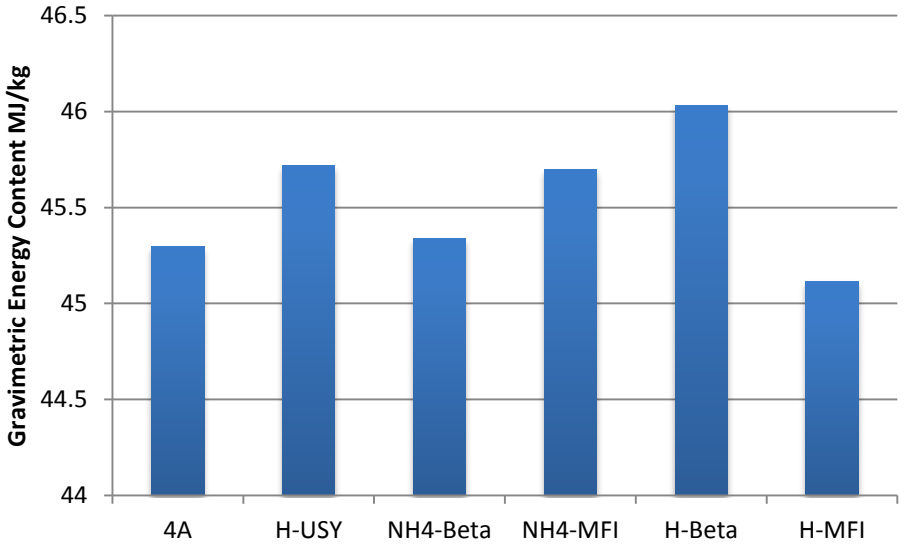


Figure 4.5-3: Gravimetric energy density of distillate products for each of the zeolite catalysts.

With respect to gravimetric energy density, all the distillate products would be acceptable as either a road or air transport fuel. Additionally, due to the high energy density of these fuels, they could be used for blending with less energy dense fuels in order to attain minimum specification requirements.

4.5.4 Flash Point Temperature

The flash point temperature of a fuel, is the temperature at which a combustible fuel/air vapour mixture forms above the bulk fuel liquid. For more volatile fuels, this tends to occur at a lower temperature and for less volatile, a higher temperature. To satisfy the flash point criteria for road transport diesel, and Jet A-1, the fuels must have a minimum flash point temperature of 55 °C or 38 °C respectively.

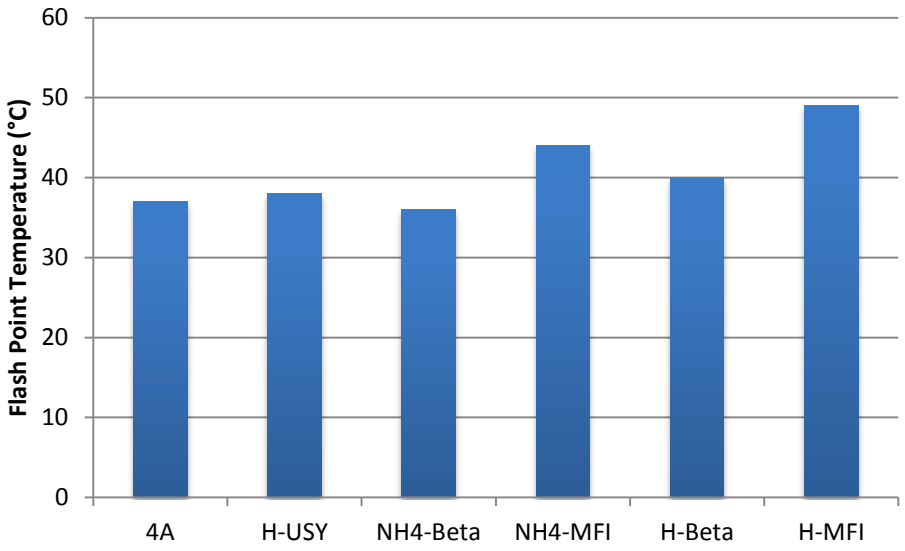


Figure 4.5-4: Flash point temperatures for distillate products for each of the zeolite catalysts.

The distillate products here possess flash point temperatures between 36 °C and 49 °C (Figure 4.5-4). All products satisfy the flash point criteria for Jet A-1 except zeolite 4A and NH_4^+-Beta which have flash point temperatures 1 and 2 °C respectively, below the minimum. All fuels have a flash point temperature of below 55 °C and as such do not satisfy the European specification for diesel fuel. The low flash point temperatures exhibited by these fuels are indicative that a substantial proportion of the fuels produced consists of relatively short chain, and volatile compounds.

4.6 CONCLUSIONS

Over the course of this investigation, the newly reported Liquid Phase Pyrolysis (LPP) reaction was investigated for its suitability in the conversion of a pistachio nut waste stream into a useable biofuel for use as a liquid transport fuel.

Primarily the original catalyst proposed for this reaction, the Zeolite 4A AlphaKat was investigated. Whilst the catalyst is active with respect to conversion of pistachio hulls to a liquid product, cracking of the hydrocarbon carrier oil was favoured, with only approximately 7 mol% modern (bio-derived) carbon being detected in the distillate products. This equated to approximately 40% of the available carbon in the biomass partitioning into the fuel. The catalyst was found to deactivate completely after first use, not allowing for the possibility of reuse without a regeneration step. This would severely impact on the economics of the process when run on a larger scale, not only in procurement costs, but also waste processing. In light of this, other catalysts were investigated for activity.

It was found that the use of a range of zeolite catalysts was effective for the conversion of biomass-derived compounds into a liquid product. The catalysts exhibit varying selectivity for the biomass derived species present within the refined hydrocarbon carrier oil. The simultaneous cracking of carrier oil alongside the conversion of bio-derived compounds yields fuel mixtures which are largely comprised of fossil oil derived carbon. Modern carbon content, present as a result of biomass conversion, was determined for all experiments using ^{14}C analysis. The highest proportion of modern carbon was found in product mixtures produced using the zeolite H-USY, however, on reuse this catalyst showed a large reduction in activity. While generally all the catalysts were more active, the maximum carbon partitioned from the biomass into the fuel was 40% of that available.

When using the standard AlphaKat zeolite, the proportion of biomass derived distillate reduced when biomass was added in small quantities throughout the reaction. This, combined with biomass free ‘catalyst only’ experiments demonstrates that the presence of biomass has a co-catalytic effect and biomass loading may be one of the primary factors in determining the proportion of biofuel produced.

Catalyst lifetime was found to vary considerably amongst the catalysts tested, with AlphaKat zeolite showing no activity upon 2nd use. The other catalysts tested all retained some activity, with MFI based frameworks appearing to perform best after

the first use, and H-USY showing the highest catalytic activity and specificity, but with greater deactivation observed upon reuse. Overall, H-MFI appeared to possess a combination of relatively good selectivity coupled with average efficiency and good reusability, with little reduction observed upon reuse without any regeneration step needed.

4.7 EXPERIMENTAL

4.7.1 Standard Liquid Phase Pyrolysis Reaction

A 1L (316 stainless steel) stirred autoclave was charged with 100g hydrocarbon carrier oil (minimum boiling point >180 °C). To this oil was added 20g of catalyst, 20g of pistachio hull biomass (<3mm) and 2g calcium hydroxide neutraliser. The reaction was stirred at 300 rpm and heated to 250 °C at a ramp rate of 4.17 °C/min. The reaction was held at this temperature until the reaction ceased to produce product distillate; typically 4 hours. Product distillate was collected after each hour of reaction and the mass recorded. Remaining solids were recovered through filtration under reduced pressure, washed with 3 x 150 mL $CHCl_3$ and dried at 80 °C overnight.

4.7.2 Temperature Variation Reactions

The same method was used as as presented in 5.8.1, however temperature was held at 150 °C, 250 °C (as in standard reaction) and 300 °C.

4.7.3 Staged Biomass Loading

A 1L (316 stainless steel) stirred autoclave was charged with 100g hydrocarbon carrier oil (minimum boiling point >180 °C). To this oil was added 20g of catalyst. The reaction was stirred at 300 rpm and heated to 250 °C at a ramp rate of 4.17 °C/min. The reaction was held at this temperature for 4 hours. At one hour intervals starting at 1 hour into the reaction, 5g portions of biomass were added to the reaction through a sample port. Product distillate was collected after each hour of reaction and the mass recorded. Remaining solids were recovered through filtration under reduced pressure, washed with 3 x 150 mL $CHCl_3$ and dried at 80 °C overnight. $CHCl_3$ was removed from the remaining carrier oil/washings by rotary evaporation.

4.7.4 Analysis

Remaining reaction solids were analysed by elemental analysis and Thermogravimetric analysis using a Setaram TG-92 thermogravimetric analyser. A ramp rate of 10 °C/min was used to 1000 °C with a 10 minute isotherm at 150 °C.

Liquid products were analysed by ^1H NMR (Agilent 500MHz).

4.7.5 Fuel Properties Measurements

4.7.5.1 Kinematic Viscosity

Kinematic viscosity was determined in line with ASTM D445. A Cannon-Fenske routine kinematic viscometer, size 150 was used. Test temperatures were maintained using a stirred water bath. Samples were allowed to rest in the water bath for at least 10 minutes prior to commencement of the test, to allow for temperature equilibration.

4.7.5.2 Flash Point temperature

Flash point temperature was determined in accordance with ASTM D56. A Seta Semi-Automatic Tag Flash Point Tester was used. A minimum of 8 mL of sample was used to ensure formation of a fuel-air mixture. A heating rate of 2 °C/min was used, with water being replaced for each use and a starting temperature of approx. 17 °C being used.

4.7.5.3 Higher Heating Value (HHV)

Higher Heating Value was determined using an IKA C1 oxygen bomb calorimeter. The machine was calibrated with benzoic acid of known calorific value prior to use.

4.7.5.4 Melting Point Temperature

Melting point temperatures were determined using a low temperature freezer. Temperatures were varied at 1 °C intervals, with equilibration time of 3 minutes at each temperature. The sample was deemed to have frozen at the point that inversion of the sample vial did not cause movement of the sample.

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Chapter 5

SMALL SCALE GAS TURBINE TESTING OF THE NOVEL FUEL BLENDS

5.1 INTRODUCTION

With increasing pressures, both legislatively and economically arising from better awareness of the environmental impact of aviation, there is growing focus on the production of alternative jet fuels. Specifications for jet fuels describe in some depth the physical properties of conventional jet fuels, however there continues to be a need for verification of their suitability through engine testing. Testing on full-scale aircraft engines is hugely costly, slowing the progress of potential alternative fuels from theoretical and lab based development to secondary more empirical evaluation through combustion in an engine. In this investigation, a Micro Gas Turbine (MGT) was used as a cost efficient, and rapid method of evaluation for the most suitable fuels reported previously in this study.

MGTs are commonly used in power generation units for small-scale power production.[1-3] Previous research into the operation and emissions of micro gas turbines has generally therefore been directed towards this end use.[4-10] The investigation of potential bioderived fuels in the context of engine and performance testing, has until recently focused on testing using internal combustion engines with a large portion of the research literature devoted to investigating the effect of using 1st generation oxygenated biofuels, such as fatty acid methyl esters (FAMEs) derived from various plant and animal fat derived oils.[11-14] Whilst these studies can indicate general characteristics of fuels that may be relevant to aviation fuels, there is a need for much more extensive testing using engines and fuels that better replicate the operational characteristics of an aviation gas turbine engine.

The use of micro gas turbines for the investigation of aviation fuel provides a reliable route to quickly analyse the effect of alternative aviation fuel formulations on the operation of a real engine, rather than inferring likely effects from previously reported studies which instead focus on static power generation units.[11, 15, 16] In the few studies that have been conducted within the area of aviation fuel-biofuel testing in gas turbines, it has commonly been found that whilst biofuels do not exceed the performance of conventional jet fuel, at blend levels of up to 50% they tend to provide performance analogous to that of conventional jet fuel.[17] A small reduction in CO is also commonly reported, and in some cases a reduction in NOx emissions.

In this investigation a number of proposed alternative aviation fuels were blended with conventional Jet A-1 aviation fuel at a 50 vol% blend level. In order to ascertain the

magnitude of deviation caused by incorporation of the surrogates, with respect to a few key emissions measurements.

5.2 AIMS

The aim of this work is to ascertain the effect on performance and emissions characteristics in a Mercury HP micro gas turbine, of blending at a 50 vol% level, Jet A-1 a conventional aviation fuel, with a host of alternative iso-alcohol derived oxygenated fuels and bio-catalytically produced alkane model compounds discussed earlier in this thesis. Results are presented at four throttle settings and results discussed in the context of likely applicability to real world performance.

The suitability of the experimental engine rig is also discussed, particularly in reference to previously conducted fuel testing from the literature, which commonly utilise micro gas turbines designed for power generation applications, rather than purpose built engines for aeronautic applications, as is used in this investigation.

5.3 EXPERIMENTAL

An AMT Mercury HP E-start micro turbine engine was used in this investigation. These engines are conventionally used for powering large model aircraft, and unmanned aerial vehicles. They are ideally suited to testing experimental fuels due to their low fuel demand coupled with a good replication of the operation of larger engines.

Table 5.3-1: Manufacturer's specification for Mercury HP micro turbine engine

Mercury HP gas-turbine.

	E-start system		Air-start system	
Diameter	100	mm	100	mm
Length	292	mm	220	mm
Turbine weight	1550	gram	1400	gram
System weight *	2235	gram	2005	gram
Thrust @ max. rpm	88	N	88	N
Thrust @ min. rpm	4	N	4	N
Maximum RPM	151,900		151,900	
Idle RPM	47,600		47,600	
Pressure ratio @ max. rpm2,8 :1			2,8 :1	
Mass flow @ max. rpm	250	gr/sec.	250	gr/sec.
Normal EGT	650	C	650	C
Maximum EGT	750	C	750	C
Fuel consumption @ max. rpm	295	gr/min.	295	gr/min.
Fuel	JP-4/petroleum/Jet A1			
Oil	4,5% aeroshell 500 mixed with fuel.			

The engine, of the type shown in (Figure 5.3-1) has a single stage compressor which is connected via a central drive shaft to a turbine at the rear of the engine. The manufacturer's specification is shown in (Table 5.3-1). Whilst not strictly representative of all elements of a large aviation gas turbine engine, the principles of fuels combustion in a micro turbine are the same as those in a full size turbine, as such it is reasonable to expect that any observations would likely be scalable, and at the very least, allow for comparison of the alternative fuels relative to one another.

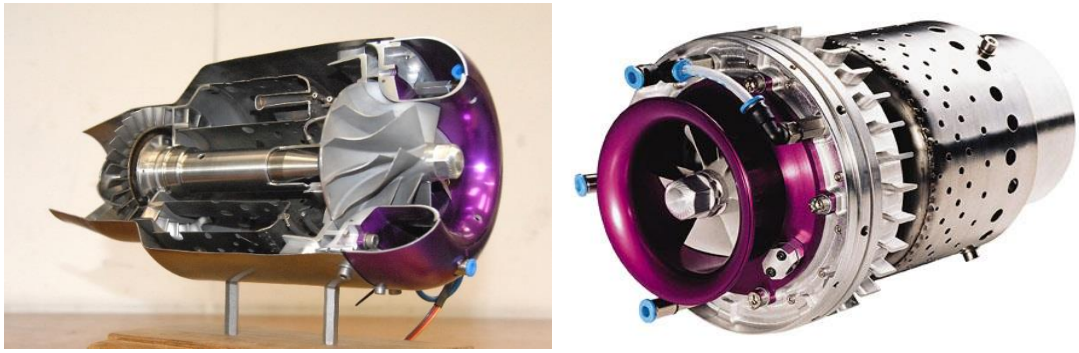

Figure 5.3-1: left) cutaway of Mercury HP engine (right) Mercury HP engine without outer cover showing air flow mechanism

Jet A-1, an industry standard aviation fuel, was obtained from project partners at Airbus, a leading UK aircraft manufacturer. Jet A-1 was blended with all experimental fuels at a 50 vol% level before testing. Fuels were shaken, and checked visually for miscibility.

Once blended, 100 mL of each fuel blend was transferred to a 250 mL Duran™ bottle, with a fuel line inserted through the cap.

5.3.1.1 IAP fuels (Chapter 3):

IAP fuels are those experimental fuels as described in Chapter 3 of this thesis. They are the product of a palladium catalysed alkylation of acetone and isoamyl alcohol to produce alcohol and ketone products ranging from 5 through to 13 carbon chain lengths.

5.3.1.2 IBP fuels (Chapter 3):

IBP fuels are again described in depth in chapter 3 of this thesis, however these fuels have been produced in a manner analogous to that of the IAP process, with the replacement of isoamyl alcohol with isobutyl alcohol.

5.3.1.3 10-12 carbon alkane fuels (Chapter 2):

Decane and dodecane have been used here as a model for the fuel which, as suggested in Chapter 2 of this thesis, could be produced from the conversion of furanic compounds through a room temperature, ambient pressure enzymatic catalysis process.

5.3.2 Engine Rig Setup

The engine was mounted in a heavy scaffold frame, capable of resisting the 8kg maximum thrust of the engine without loss of stability. The engine is mounted on a pole within the frame which is allowed to pivot at the base. The pole is allowed to rest against a piezoelectric load cell, which is calibrated for loads of 0 to 10 kg. This load cell was configured to give a value for thrust measurements alongside emissions measurements.

Emissions measurements were obtained using a Horiba MEXA-7000 emissions analysis apparatus, a road transport industry standard emissions analysis system. The system relies on Gas Chromatography for identification of species within the sample gas.

Control of the engine was achieved through reconciliation of the supplied engine control unit (ECU) software with the local control software, CADET.

A PTFE emissions sampling line was connected to a nose cone designed and manufactured at the University of Bath. This allowed emissions sampling directly from the exhaust without the incorporation of entrained ambient air, and without the need for irreversible modification of the engine itself. Sampling of exhaust gases was effected at a flow rate of between 9 and 13 L/min, allowing for analysis of even low concentration emissions. Delay between sampling at the engine and analysis was measured to be between 5 and 6 seconds. High flow and short delay between sampling and analysis minimised losses through condensation within the sample line.

5.3.3 Testing & Repeatability Measurements

The rig operation protocol and emissions testing parameters were optimised using conventional aviation fuel, in an engine test cell located in the Powertrain and Vehicle Research Centre at the University of Bath, using active extraction of exhaust gases (Figure 5.3-2).

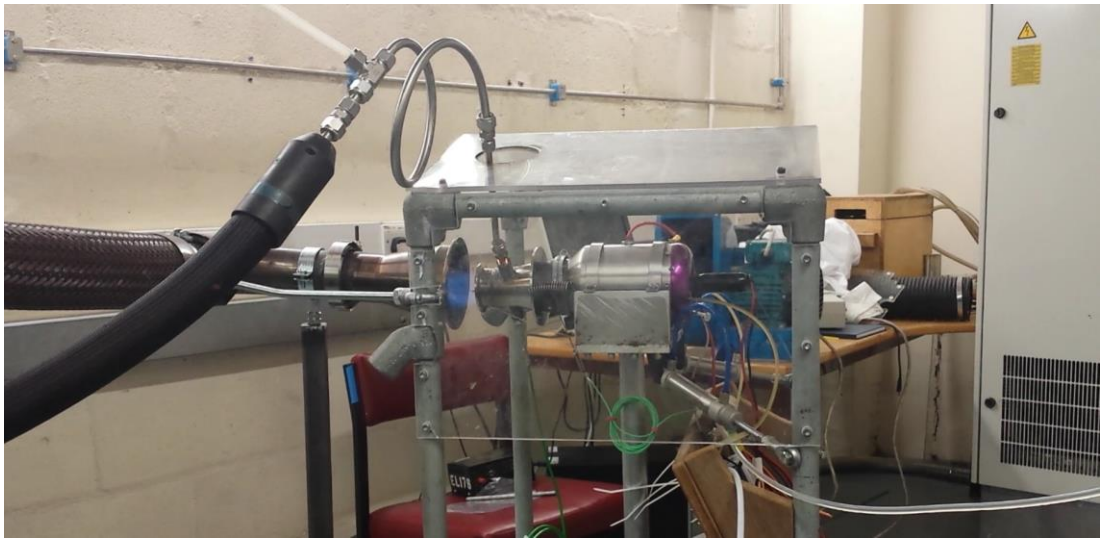

Figure 5.3-2: photograph of engine in preliminary testing using active extraction

After preliminary testing and repeatability measurements, the use of active exhaust extraction was abandoned due to the presence of the receiving cone causing back pressure and loading the engine. This in turn causing over-heating and automatic shutdown. Another effect of the back pressure was to cause increased turbulence in the flow of exhaust gases, leading to irregular emissions readings.

It was found that with removal of the exhaust cone the overheating and turbulence was alleviated, meaning the engine was able to complete the test sequence and give accurate and repeatable emissions measurements. The engine was assembled in a chassis dynamometer test area, with the exhaust being directed to atmosphere, with just an open sampling cuff placed at the engine exhaust (Figure 5.3-3).

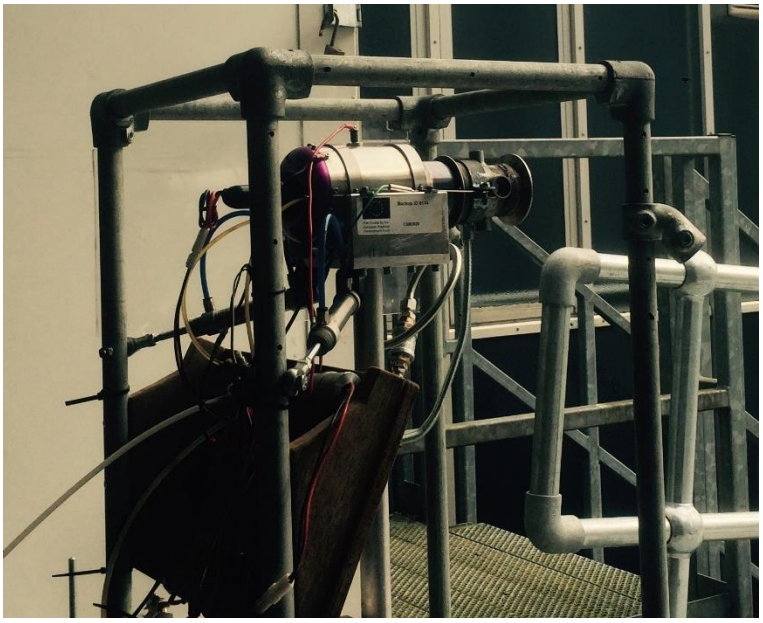

Figure 5.3-3: photograph of the engine placed in the chassis dynomometer facility, venting to atmosphere.

The engine was controlled from a separated control area adjoining the test area, using the facility control system to run a pre-optimised script in order to obtain well replicated engine operations during testing.

CADET software package was used as a control system for the facility, and so the script was loaded onto this control software to allow for reliable reconciliation of emissions output and control inputs.

The engine was started according to the manufacturer's instructions, with initial start-up using propane gas from a gas cylinder. Once the engine had ignited and stabilised using the propane gas, pumping of liquid fuel initiated. Upon ignition of the liquid fuel, propane flow was stopped. After 30 seconds of running on liquid fuel at idle (0% throttle), the engine was deemed to be running at a steady state condition and the test script initiated (Figure 5.3-4).

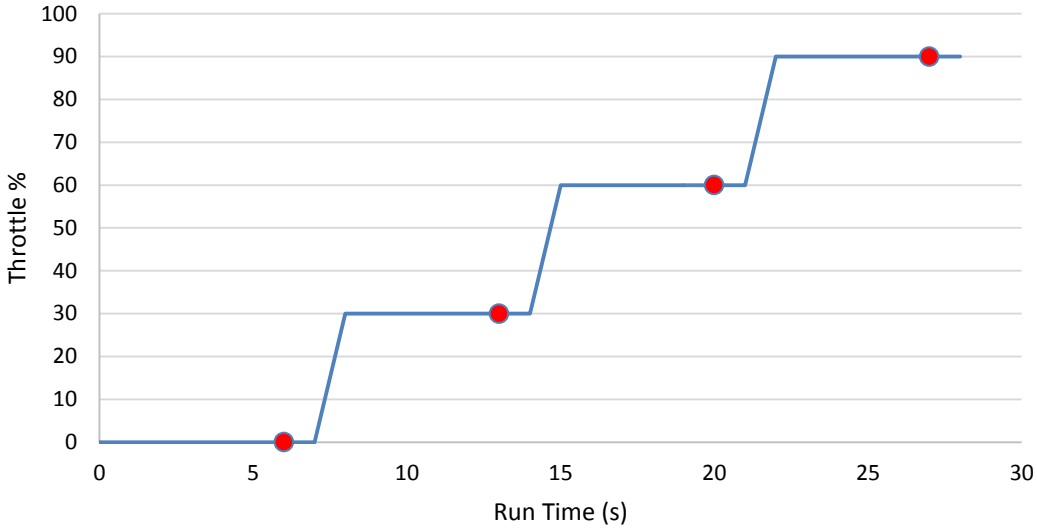

Figure 5.3-4: Graphic representation of the engine test run script with sampling points shown in red.

A seven second equilibration time was found to be sufficient to allow for fluctuations in emissions measurements to settle, and minimised the amount of fuel necessary for each test. For each measurement, a single value, 6 seconds into each plateau for each throttle setting was selected for data compilation and analysis. Emissions, turbine speed, exhaust gas temperature and thrust measurements were all delivered through dedicated channels to the CADET logging software.

Upon completion of the test, the engine was allowed to go through a pre-programmed shut down sequence, before being allowed to cool to room temperature before the commencement of subsequent tests. Fuel lines were emptied and rinsed with Jet-A1 to ensure no cross contamination between test fuels.

5.3.4 Error Determination

All errors used in emissions analyses in this chapter have been determined from repeated testing of Jet A-1 using the cycle described. The standard deviation of these measurements was determined and applied as a standard error. Error shown applies only to the experimental variability.

5.4 RESULTS & DISCUSSION

5.4.1 Fuel properties

The main fuel properties determined in the previous chapters are given in Table 5.4-1.

Table 5.4-1: Measured fuel properties of experimental fuels

	HCV	Flash Point Temperature	Viscosity (-20)	viscosity (20)	Melting Point Temperature
IAP120	37.401	<5	11.257	2.735	-71
IAP140	39.278	49	31.727	4.814	-68
IAP160	30.442	45	21.331	4.207	-71
IBP120	36.212	33	12.562	2.92	-71
IBP140	35.547	35	16.839	3.427	-71
IBP160	36.112	35	16.382	3.524	-71
dodecane	47.307	71	frozen	1.936	-7
decane	46.852	47	2.927	1.269	-26
jetA-1	45.689	43	3.954	1.58	-56

Low temperature properties are particularly affected by the presence of moieties that allow for strong intermolecular forces, particularly hydrogen bonding. The expected trend of higher viscosity at low temperatures for the oxygenate fuels is observed.

The higher calorific value (HHV) is one of the most important properties of a jet fuel, limiting the range of any aircraft. The HHV of a fuel is the amount of energy that is released when combusting a known amount of any given fuel. Generally the calorific value will increase with an increasing proportion of C-H bonds in the fuel molecules. Therefore the higher the H:C ratio of a fuel, the higher the HCV will tend to be. While oxygenated fuels can vary from this principle, the fuels presented here generally adhere to this principle, with oxygenate fuels showing a marked decrease relative to the hydrocarbon counterparts.

An important safety consideration is the flash point of the fuel. The flash point temperature is the temperature at which, in an enclosed space a flammable fuel air mixture forms above the bulk fuel. This is tested in a dedicated closed cup flash point testing machine, where the fuel air vapour is periodically exposed to a naked flame until a flash is obtained. The Flash point temperature is, in general, dependent on whether there are enough volatile components to form a flammable mixture at lower temperatures. In the case of IAP120, there is evidently a much higher proportion of

flammable and highly volatile compounds within the fuel, leading to a much reduced flash point temperature of less than 5.

Melting point temperatures are much more difficult to predict, with more complex intermolecular interactions to consider. Low melting point compounds in relatively low concentrations can have a disrupting effect on the intermolecular forces of a potentially higher freezing temperature bulk fuel. The melting point is however easily determined using a low temperature, programmable freezer.

5.4.2 Thrust

Gas turbine engines work according to the 'Brayton cycle' as shown in Figure 5.4-1 where air is drawn into the engine (1) compressed and mixed with injected fuel (2). This fuel air mixture is then ignited, and combustion products formed, thus increasing the volume of the gases. This gas, at increased temperature and pressure is then ejected from the engine (3), driving a turbine, which in turn drives a compressor. In an open system as in with aviation gas turbines, exhaust gases are expelled to atmosphere (4).

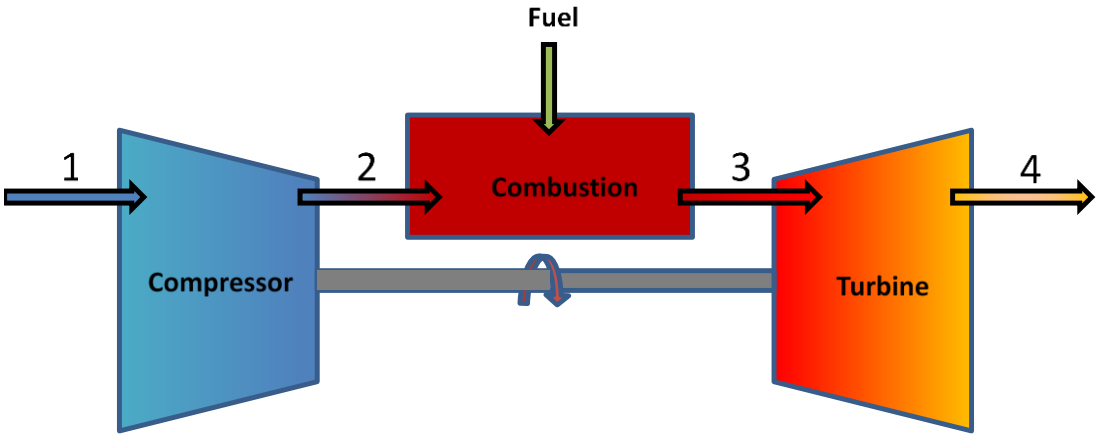

Figure 5.4-1: Schematic representation of an open system gas turbine engine operating as described by the Brayton cycle

The amount of thrust for any given gas turbine engine at constant ambient pressure and temperature is dependent on the ratio of expansion achieved as a result of combustion of the fuel air mixture within the combustion section of the engine. When comparing different fuels in the context of gas turbine utilisation, the difference in thrust will come as a result of differing quantities and volumes of combustion products. The combustion chemistry of the fuels may also differ depending on differences in vaporisation temperatures, and spray pattern characteristics affecting vaporisation.

In this investigation, the thrust produced by the engine when using the various fuels tested was measured by a piezoelectric load cell, calibrated and configured in order to give a value alongside other testing parameters in the 'CADET' dynamometer software.

It was expected that the alternative fuels would combust in a manner analogous to Jet A-1 and produce similar amounts of thrust for a given throttle input, potentially with a small decrease in thrust for oxygenated fuels owing to their reduced HCV as determined by fuel properties testing conducted prior to engine testing, and in line with previous investigations into alternative gas turbine fuels.

Primarily the thrust was measured at idle, 0% throttle input, (Figure 5.4-2). Under these conditions Jet A-1 produces 1.38 kg of thrust.

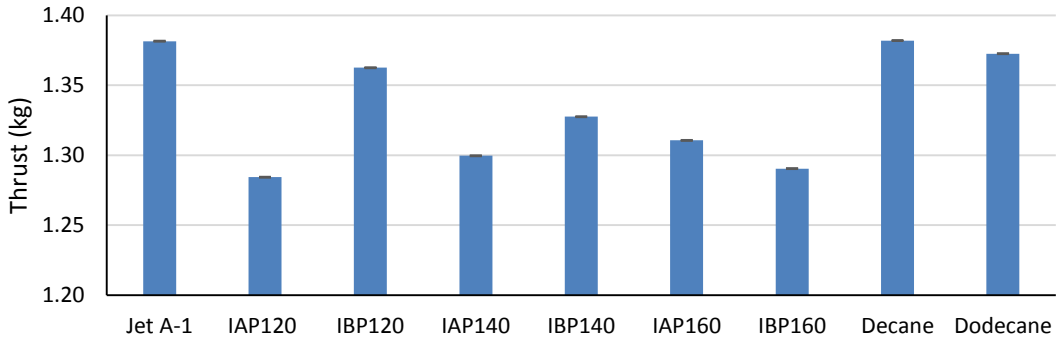

Figure 5.4-2: Thrust at idle. Standard error from repeatability test applied

The two hydrocarbon fuels decane and dodecane, that could be produced from furfural and 5-HMF respectively, produced comparable amounts under the same conditions with decane producing 1.38 kg and dodecane producing 1.37 kg. The next highest thrust value observed is when using the IBP120 fuel blend. With the other oxygenates producing significantly lower thrust than this. The high thrust values of the hydrocarbons at idle correlate well with the associated HCV values for each of the fuels, however, IBP120 possesses a similar calorific value to the other oxygenate fuels, demonstrating that it is not just the calorific value of a fuel which is important in determining its suitability and efficiency as a jet fuel alternative, but also the complex interactions between conventional and alternative fuels and atomisation and combustion characteristics unique to each fuel blend. These differences may arise through differences in viscosities or volatilities at the point of injection, leading to quicker, more efficient burning. Results for thrust measurements at different throttle settings ranging were then tested from 30 % to 90 % throttle input (Figure 5.4-3).

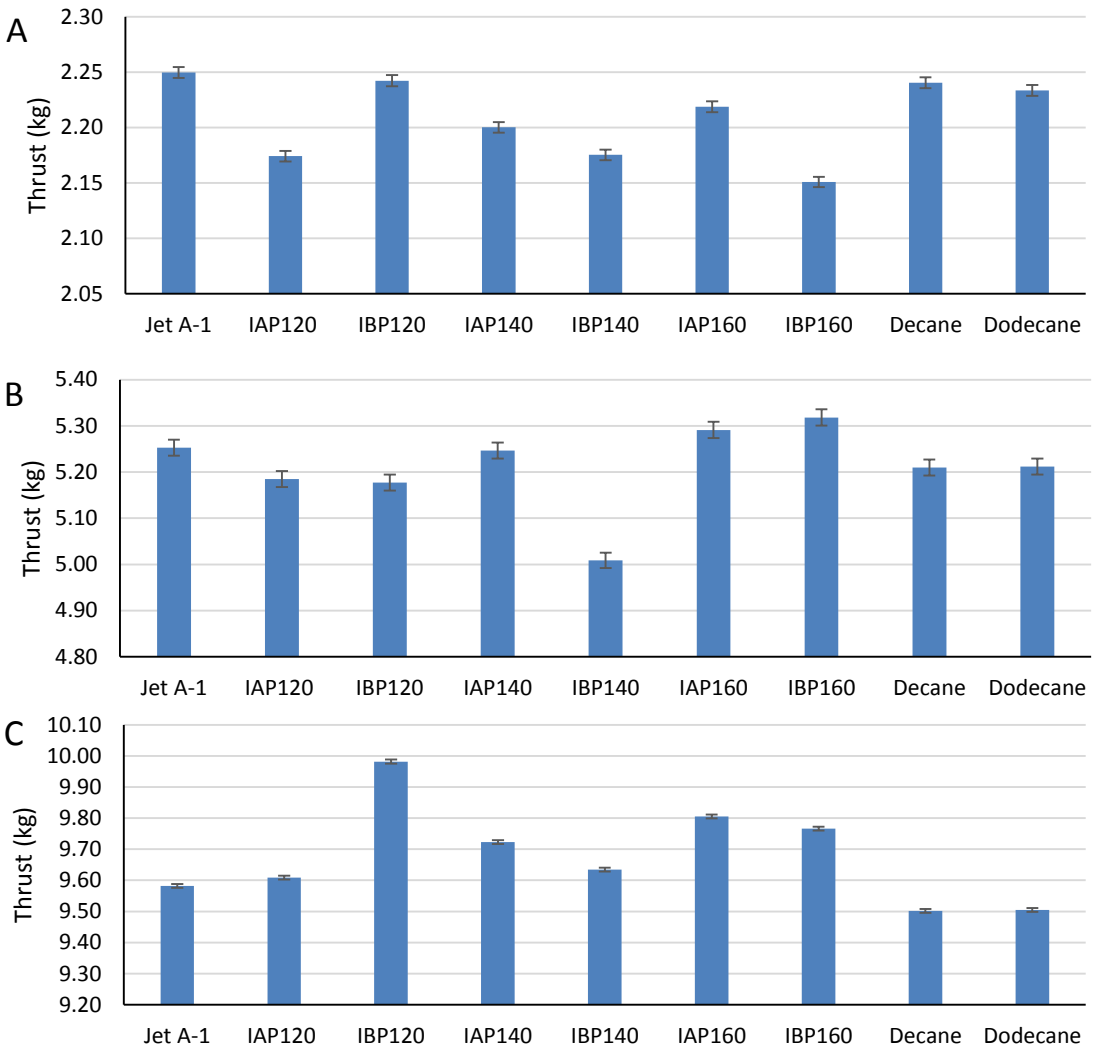

Figure 5.4-3: Thrust measurements at 30, 60 and 90 % throttle (A, B, and C, respectively). Standard error applied from repeatability testing using Jet A-1.

At 30% throttle the amount of thrust produced is increased, this is expected as the throttle modulates fuel delivery, the quantity of which in turn determines the quantity of combustion products formed, and thus, thrust. Interestingly, the increased thrust observed for the hydrocarbons relative to the oxygenates is largely diminished. At 30 % throttle, Jet A-1 exhibits the highest thrust value, providing 2.25 kg of thrust with decane and dodecane providing 2.24 kg and 2.23 kg of thrust respectively. IBP120 again exhibits the highest thrust value of the oxygenate alternative fuels with a thrust measurement of 2.24 kg being obtained. IAP120 exhibits the lowest thrust of all the fuels tested, possessing a thrust of 2.17 kg, 7.8 % lower than that of Jet A-1. Overall, oxygenated fuels appear to provide considerably less thrust than Jet A-1 and hydrocarbon alternatives at this throttle setting.

At 60% throttle the advantage of using the hydrocarbon fuels is considerably lower; with oxygenate fuels providing in some cases, greater thrust than the unblended Jet

A-1 and the blends containing decane and dodecane. Interestingly, at this throttle setting there does not appear to be a strong correlation between thrust and HCV. This non-correlation coincides with incidence of the highest experimental error observed of all thrust measurements tested.

At 90 % throttle setting the trend continues toward increased thrust for oxygenates over hydrocarbon fuels, with all oxygenate blends producing higher thrust values than the hydrocarbon alternatives and Jet A-1.

These findings of increased thrust amongst the oxygenate fuels are unexpected, and somewhat incongruous with previous gas turbine studies using oxygenate fuels.[18-20] For example, when using biodiesel as a diesel replacement for an industrial gas turbine, Lupandin *et al.* found that power (thrust) specific fuel consumption was greater when using biodiesel than when diesel oil was used. Biodiesel producing 2.125 kw/L compared with an output of 2.344 kw/L when diesel was used.

Rehman et al. conducted testing of biofuel and diesel blends on a Rover gas turbine IS/60 engine, designed for power generation. It was found that while running at low to medium loads diesel oil exhibited a lower brake specific fuel consumption (BSFC), at higher loads, this was matched by biodiesel and at maximum loads biodiesel showed improved BSFC.[19] This suggests that in an aviation gas turbine engine, higher thrusts may be achieved by oxygenates at high throttle settings and high rate of fuel delivery.

This assertion is contrary to the generally accepted position that oxygenate fuels will always produce less thrust, owing to their reduced HCV. The findings here, and those of Rehman et al. would seem to suggest that operating conditions of the gas turbine, not just the molecular oxygen content of a fuel, have a large impact on the optimum characteristics of that fuel.

5.4.3 Exhaust Gas Temperature (EGT)

Exhaust gas temperatures in gas turbine engines are directly affected by the quantity of fuel that is delivered to the engine and how fully it combusts, as well as its gravimetric energy density; the higher the energy content, and the more fully it is able to combust, the higher the EGT.

The EGT was measured using a K-type thermocouple situated within the exhaust cone of the engine, approximately 5 mm from the turbine blades. The EGT was examined at idle (0 % throttle), shown in Figure 5.4-4.

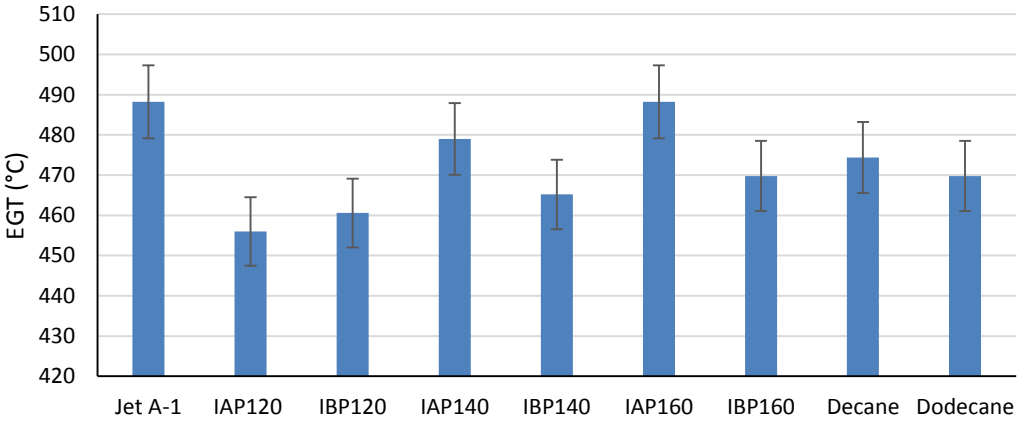

Figure 5.4-4: EGT at 0 % throttle, error bars are given as one standard deviation (n=3) based on repeats of Jet A-1

The highest temperatures were recorded when using unblended Jet A-1 which reached 490 °C, the other hydrocarbon fuels produced temperatures slightly lower than this. It was expected that the oxygenated fuels would produce lower temperatures due their lower calorific values, however during this investigation, whilst this held true for most of the oxygenates, the blend including IAP160 and IAP 140 both produced EGT values similar to Jet A1. Furthermore, the incorporation of dodecane and decane into a fuel blend appears to lower the exhaust gas temperature. This may be due to the reduction in viscosity allowing for better spray pattern and atomisation within the engine. This leads to fuller combustion that does not continue through the rear of the engine, as the fuel gradually evaporates and burns. This would cause less heating of post combustion section components and allow more rapid cooling of the exhaust gas.

The EGT was also measured at 30%, 60% and 90% throttle (Figure 5.4-5). As expected the temperature recorded at higher throttle settings was increased, due to greater quantities of fuel being burned resulting in increased heat expulsion in the exhaust. At 30% throttle, Jet A1 recorded an EGT of 502°C, as with the idle running, the oxygenated fuels also gave lower values aside from IAP160 which was comparable to the Jet A1. IBP140 produced the lowest value at 502 °C, 27 °C below that of unblended Jet A-1. This low value corresponds with one of the lowest thrust levels observed at this throttle setting. Both decane and dodecane gave EGT values within 10 °C of the unblended Jet A-1. At 30 % there does appear to have been good

correlation between observed thrust levels and exhaust gas temperatures, suggesting that with greater heat produced by combustion within the engine comes more thrust.

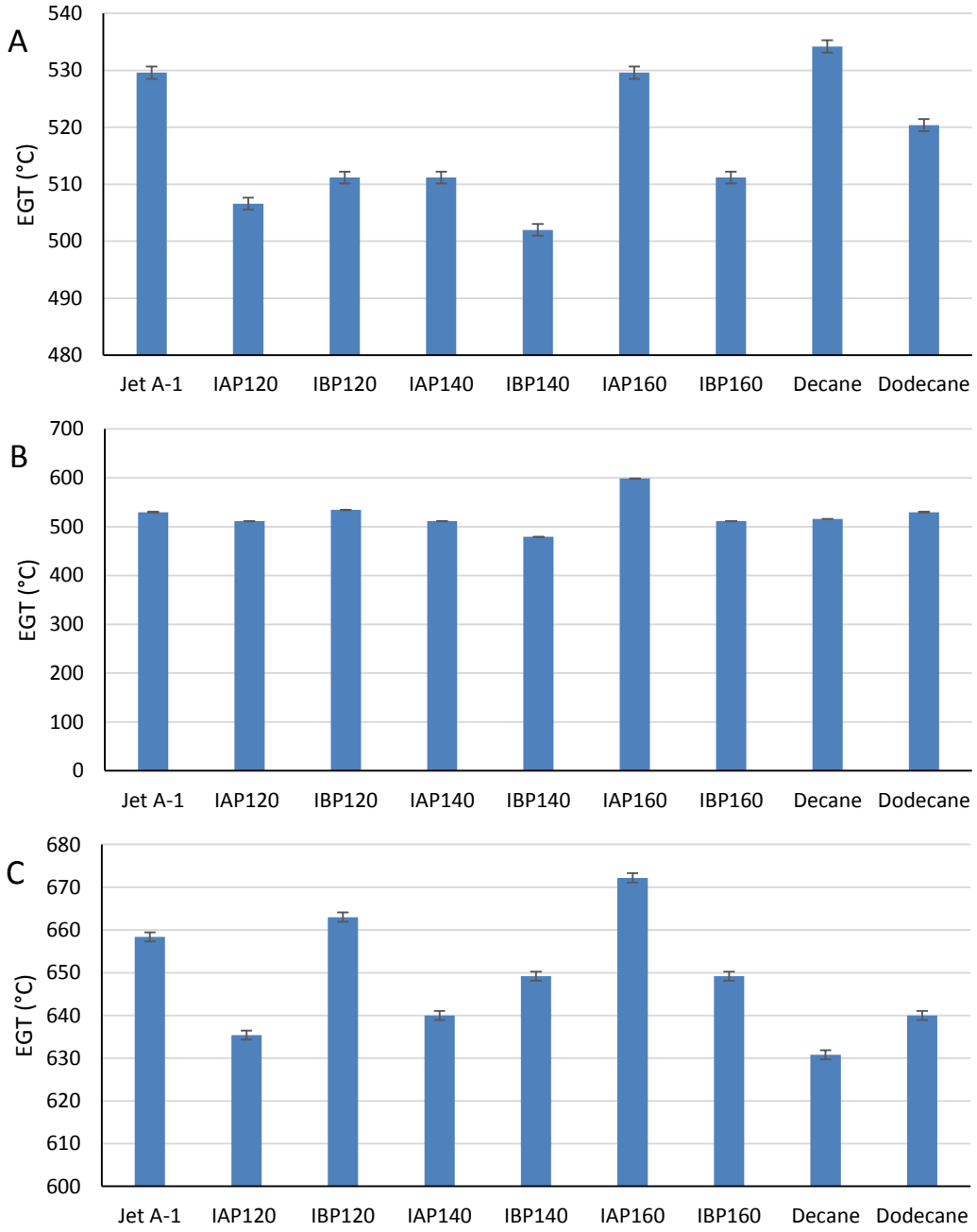

Figure 5.4-5: Exhaust gas temperatures at 30, 60 and 90 % throttle (A, B and C, respectively), error bars are given as one standard deviation (n=3) based on repeats of Jet A1

At 60 % throttle, EGT values stabilised and are similar to that of Jet A1. Decane and IAP160 exhibit reduced EGT values, whilst other fuels show increased values relative

to 30 % throttle. The results at this throttle setting are particularly important, as this is the closest approximation to a 'cruise' throttle setting at which a commercial aircraft would spend the majority of its time whilst in flight, and therefore the throttle setting at which the majority of the fuel would be combusted. IAP160 was shown to produce higher temperatures than any other fuel. Whilst this would seem to suggest a high heat of combustion, this is not supported by independent ex-situ measurement. Combination of the thrust data with the HHV value of 30.442 (compared with that of Jet A-1 at 45.689) would suggest that there may be a delay in the combustion of the fuel providing heat release in the exhaust cone, and potentially additional thrust through further expansion. Whilst no 'after burn' was observed during testing, this was not one of the parameters under investigation, and so may have occurred without observation.

At 90 % throttle input, where a high proportion of fuel is being fed into the engine, the exhaust gas temperature increases to over 600 °C. This is due to an increase in the mass of fuel that is needed for the engine to operate near its maximum thrust capability. This increase is coupled with a lower residence time within the engine and higher levels of dilution with air from the compressor. Again, IAP 160 shows higher EGT than the oxygenates and is comparable to the Jet A1. Decane and dodecane both exhibit reduced EGT values relative to the other fuels tested, and notably relative to the unblended Jet A-1. IAP160, once again, gives the highest EGT values of any of the fuels.

5.4.4 CO Emissions

Carbon monoxide emissions arise as a result of incomplete combustion of a carbon-based fuel. Incomplete combustion can occur as a result of a shortage of oxygen available within the combustion section of the engine. In reality, in a gas turbine engine there is a large excess of air relative to that required for combustion of the fuel. The atomisation and vaporisation of the fuel within the combustion section of the engine may not be perfectly efficient however, leading to the possibility of incomplete combustion.[21] The individual droplets of fuel are larger, and take longer to vaporise and form a homogeneous air/vapour mixture. This increases the proportion of time that combustion is occurring in a localised fuel rich environment around the droplets.[21] The droplet and the associated combustion region then exit the engine and are cooled and dispersed before combustion can complete.

The presence of an oxygen-containing moiety within the fuel has been shown in previous studies to aid complete combustion by increasing flame temperature, in turn reducing soot formation.[22] Limited data is available for gas turbine studies, however in a study investigating the effect of oxygenates as a combustion aid in diesel engines, it was found that increased fuel bound oxygen content generally resulted in increased CO and a reduction in particulate matter.[23] These findings are common across much of the literature, with increased CO and decreased soot formation now being a well-recognised effect of fossil fuel/ oxygenate blending.

CO was measured at idle throttle (Figure 5.4-6). The CO measured was extremely low, with little variation observed between the fuels. This suggests that all the fuels were combusting well in an air rich environment. Under these conditions, IBP120 exhibits the highest CO emissions of all the fuels tested, however there is no clear trend to suggest that the presence of oxygen within the fuel affects the levels of CO produced at low throttle. No relationships between the properties measured and levels of CO could be drawn. It is notable, however, that unblended Jet A-1, along with IAP140 and IBP160, produced the lowest amount of CO at idle.

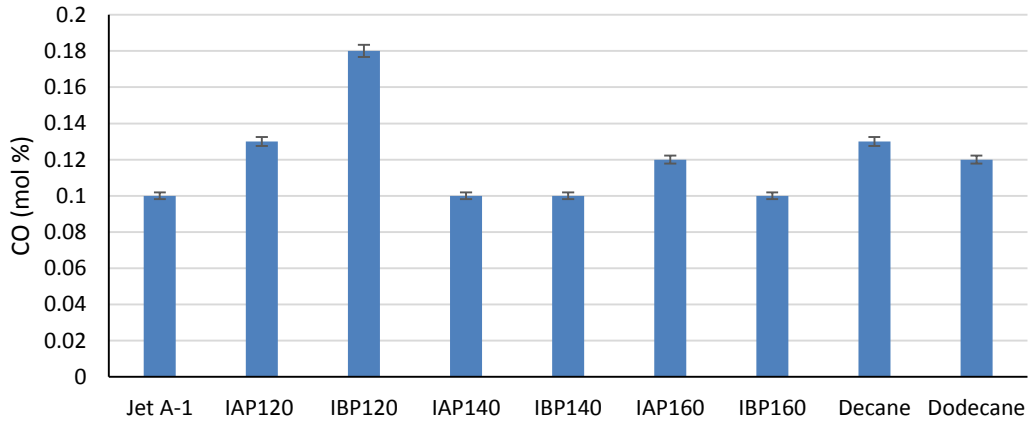

Figure 5.4-6: CO emissions at idle, error bars represent one standard deviation based on three replicates of Jet A1

It would appear that the incorporation of any of the alternative fuels tested either had no effect, or had the effect of increasing the amount of CO produced, up to 80% in the most extreme case when IBP120 was used as a blending agent.

The CO emissions were also investigated for throttle conditions of 30-90%. At 30 % the emissions are reduced slightly for all fuels, and again similar values are produced for all the fuels examined (Figure 5.4-7).

At 60 % throttle, the CO emissions are increased slightly for all the fuels, relative to the 30% throttle. All fuel blends containing iso-alcohol derived alternative fuels exhibited the same CO production as that of conventional jet fuel, with the exception of IAP120, which, similarly to the 30 % throttle test, showed a reduced production of CO. Most notably the two model hydrocarbon fuels, decane and dodecane produced a much-reduced value relative to conventional jet fuel, with a reduction of over 18 %. At this throttle condition, it would appear that a combination of increased air mass flow rate, associated with a higher compressor speed, and a more volatile fuel blend for the decane and dodecane fuels results in significantly better vaporisation and combustion. This assertion correlates well with the observed EGT values where these hydrocarbon blends exhibited temperatures amongst the highest recorded.

At 90 % throttle, where the highest volumetric proportion of fuel is fed into the engine, each fuel converges toward an average value. This is commensurate with expectations owing to more complete combustion generally occurring at higher air: fuel ratios (lean conditions) and higher combustion chamber temperatures. Combustion at this high throttle level appears to be very efficient, with very low quantities of CO being produced. It should be noted however, that small differences in CO evolution become more difficult to quantify with the equipment used due to an instrument measurement resolution of 1 ppm.

Carbon monoxide is formed as a result of incomplete combustion, and as such is indicative of poor combustion quality or inefficiency within a gas turbine. It appears that the oxygenated fuels do not increase performance in combustion characteristics, as would ethanol or biodiesel, as such the lower calorific value is not compensated for with more complete combustion.

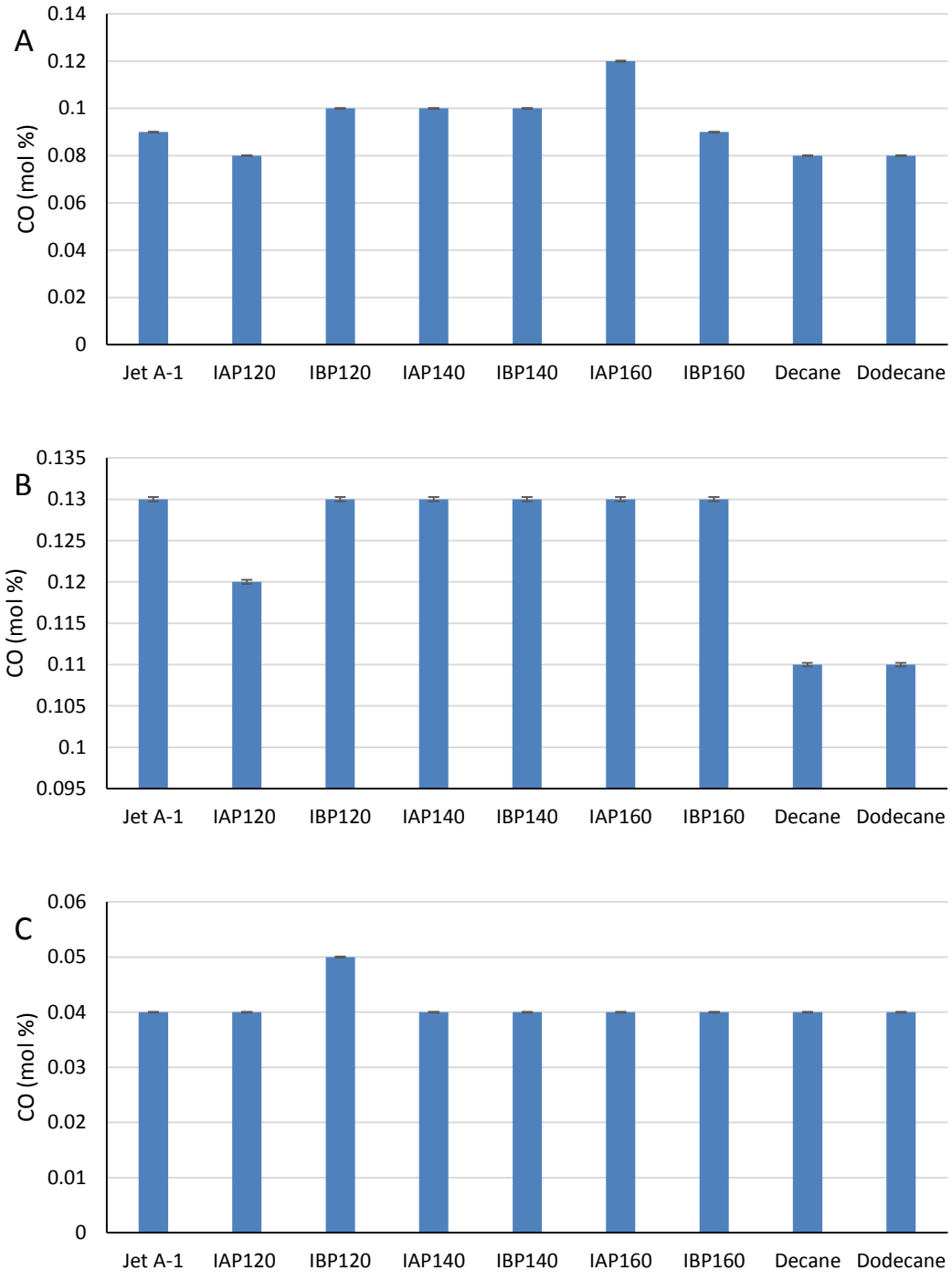

Figure 5.4-7: CO emissions at 30, 60 and 90 % throttle (A, B and C, respectively). Standard error from Jet A-1 repeatability tests applied to all measurements.

5.4.5 CO_2 emissions

As with other emissions measurements made with a gas turbine, CO_2 emissions again should only be directly compared at a given throttle condition, due to variable air fuel ratios at different compressor speeds.

At a given throttle level, a predetermined amount of fuel is delivered to the engine, by a calibrated ECU/fuel pump setup. The amount of CO_2 that is produced therefore depends on the carbon content of the fuel, and the extent of combustion.

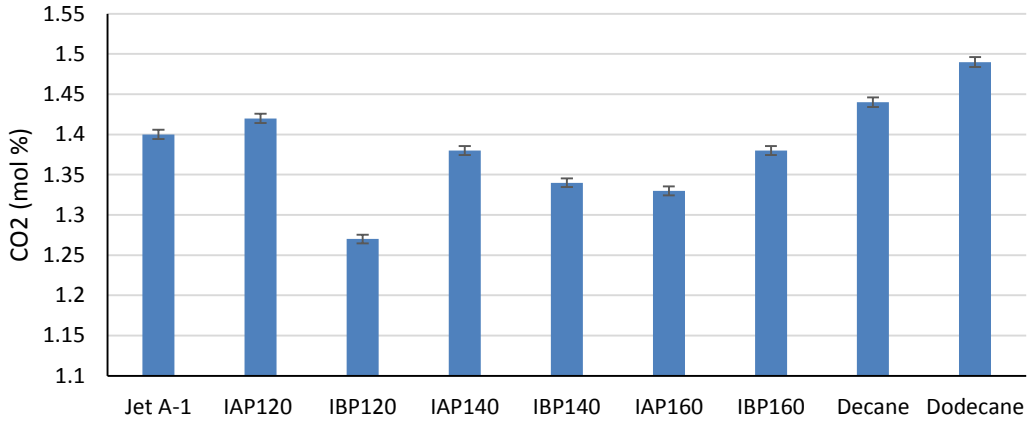

Figure 5.4-8: CO_2 emissions at 0% throttle, error bars represent one standard deviation (n=3) of Jet A1 on the system

At idle, there is appreciable variation in the amounts of CO_2 that are measured when using different fuel blends (Figure 5.4-8). Jet A-1 gives a value of 1.4 %, with decane and dodecane producing greater quantities, 1.44 and 1.49 % CO_2 respectively. Oxygenated fuels vary in their CO_2 production, with most producing lower CO_2 emissions than unblended Jet A-1, and IAP120 producing marginally more CO_2. The reason for an elevated CO_2 output when using IAP120 may be explained by better vaporisation and therefore more complete combustion. This theory is supported by reduced CO levels relative to the other oxygenated fuel blends, as well as evidence of higher levels of volatile compounds in this fuel, leading to a significantly lowered flash point relative to other fuels tested.

At 30 % throttle, CO_2 levels of the hydrocarbon fuels are reduced relative to the levels produced by the oxygenate fuels (Figure 5.4-9). This may be as a result of a higher engine temperature, allowing for better vaporisation of the less volatile oxygenate fuels. At 60 % throttle, decane and dodecane produce more CO_2 than blends containing iso-alcohol derived fuels. Jet A-1 produces a value of 1.01, with all oxygenate blends producing less CO_2 or just 1 % more in the case of IAP120.

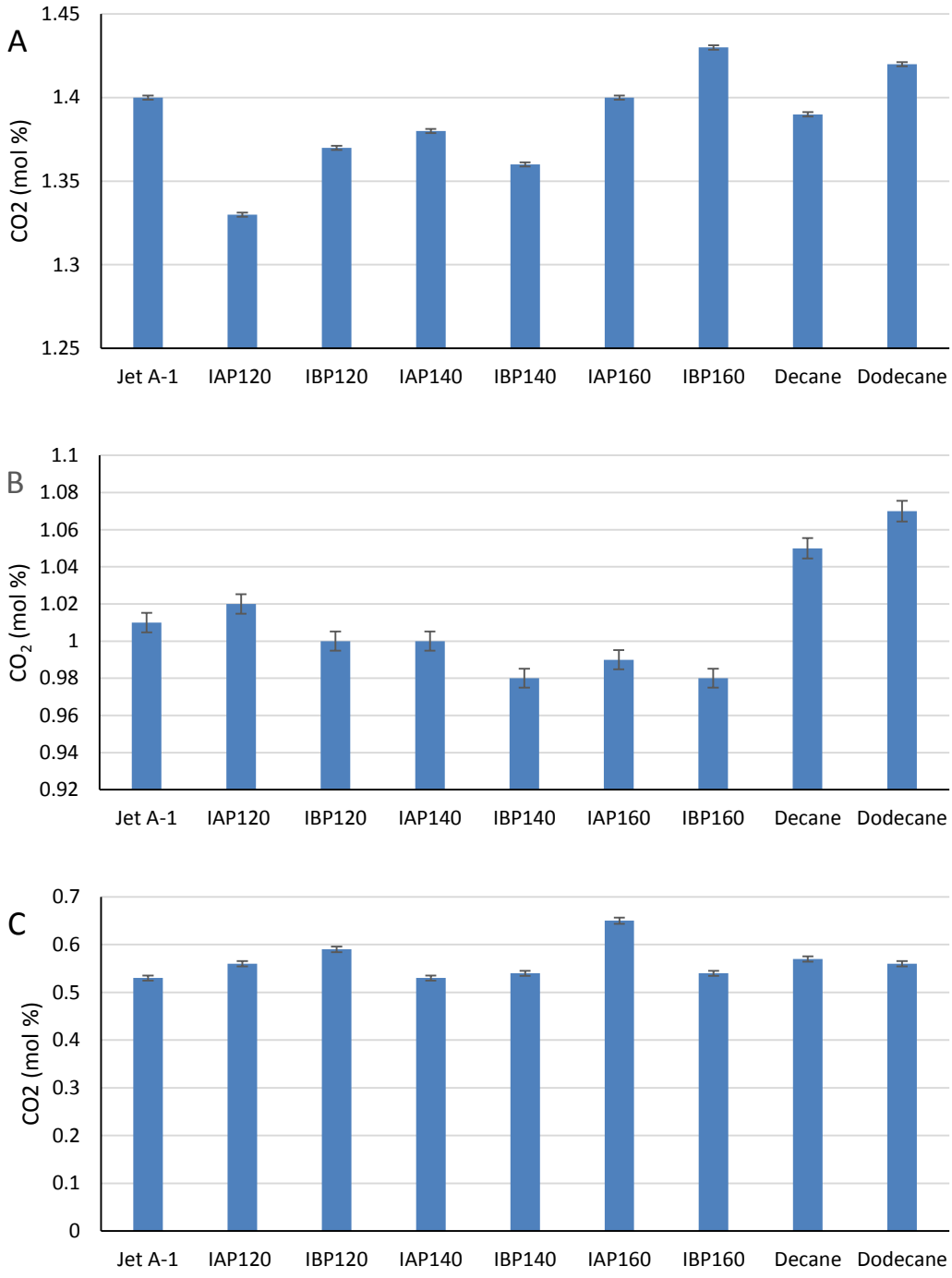

Figure 5.4-9: CO2 emissions at 30, 60 and 90 % throttle (A, B and C, respectively). Error from JetA-1 repeatability applied to all measurements as standard error.

At the highest throttle setting of 90 % oxygenate blends appear to give a higher CO_2 reading relative to hydrocarbon fuels when compared to the relative profiles at the lower throttle settings, particularly those at 60 % throttle. This increased CO_2

production, may be as a result of better vaporisation of the fuels within the combustion section of the engine at the high throttle setting, due to the availability of oxygen from within the fuel molecules.

5.1.2 Total Emissions by Exhaust O_2 Displacement

Oxygen levels in the exhaust of the gas turbine may be used in order to look at the overall production of pollutants resulting from the combustion of fuel in the engine.

All the fuels tested showed a similar trend in displaced oxygen (Figure 5.4-10). At low throttle speeds, approximately 18.5% oxygen was observed in the exhaust for all the fuels tested. Observed variations were largest at low throttle settings, with the highest displacement of O_2 occurring at idle. The largest displacement of O_2 was produced by combustion of unblended Jet A-1 and dodecane. This correlates well with observations of other emissions, and would seem to be in favour of the assertion that better quality combustion is achieved with these hydrocarbon fuels at low throttle settings. At 60 % throttle, more oxygen is present and at 90% approximately the same trend is observed, with total emissions being higher for the hydrocarbon fuels. At the highest throttle setting of 90%, all the results were of the same value within the margin of error for the equipment used.

With oxygenated biofuels in conventional compression engines, a general trend of reduced CO and EGT is evident. It is notable that although emissions appear to be higher for hydrocarbon fuels, particularly at lower throttle settings, thrust values tended to be correspondingly higher, suggesting that rather than being a more polluting fuel the hydrocarbon fuels are in fact more efficient, with no general increase observed in emissions.

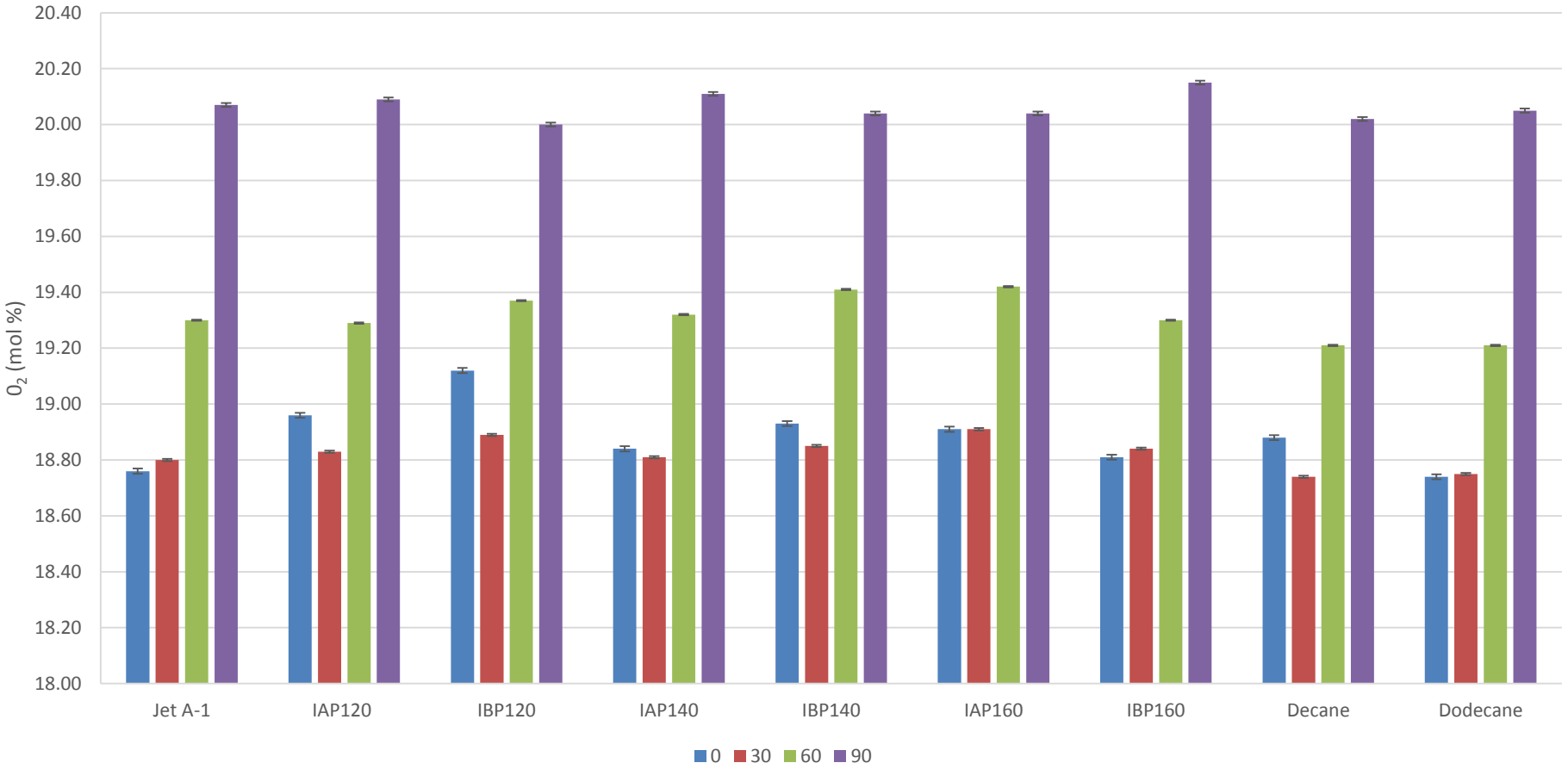

Figure 5.4-10: O_2 content of jet exhaust at throttle settings of 0, 30, 60 and 90 %, error bars are given as one standard deviation of jet A1 measurement (n=3)

Whilst it is most relevant to investigate how a fuel blend behaves when ‘dropped in’ for use without modification to the engine or fuel delivery systems, an informative metric to determine the potential of a fuel blend is that of thrust specific total emissions. To this end, the total emissions per unit thrust were calculated for each of the fuels investigated.

5.4.6 Thrust specific total emissions

The thrust specific total emissions were calculated for all the fuels over different throttle conditions and compared directly to Jet A1 (Figure 5.4-11). All non-O_2 and non-N_2 gaseous species detected were considered ‘emissions’ for the purpose of this calculation. It was observed that at lower throttle inputs variability is largest, with up to an 18 % increase in emissions per unit thrust observed for the IBP120/Jet A-1 blend. In the case of decane and dodecane for a given thrust emissions appear to be reduced in all throttle levels, other than at idle when a 6 % increase in emissions relative to Jet A-1 is observed for decane. At higher throttle inputs, there are no trends evident for the oxygenated fuels tested. This suggests that with adjustment of fuel delivery systems there may potentially be little detrimental effect logistically arising from the substitution of conventional aviation fuel with blends containing these alternatives.

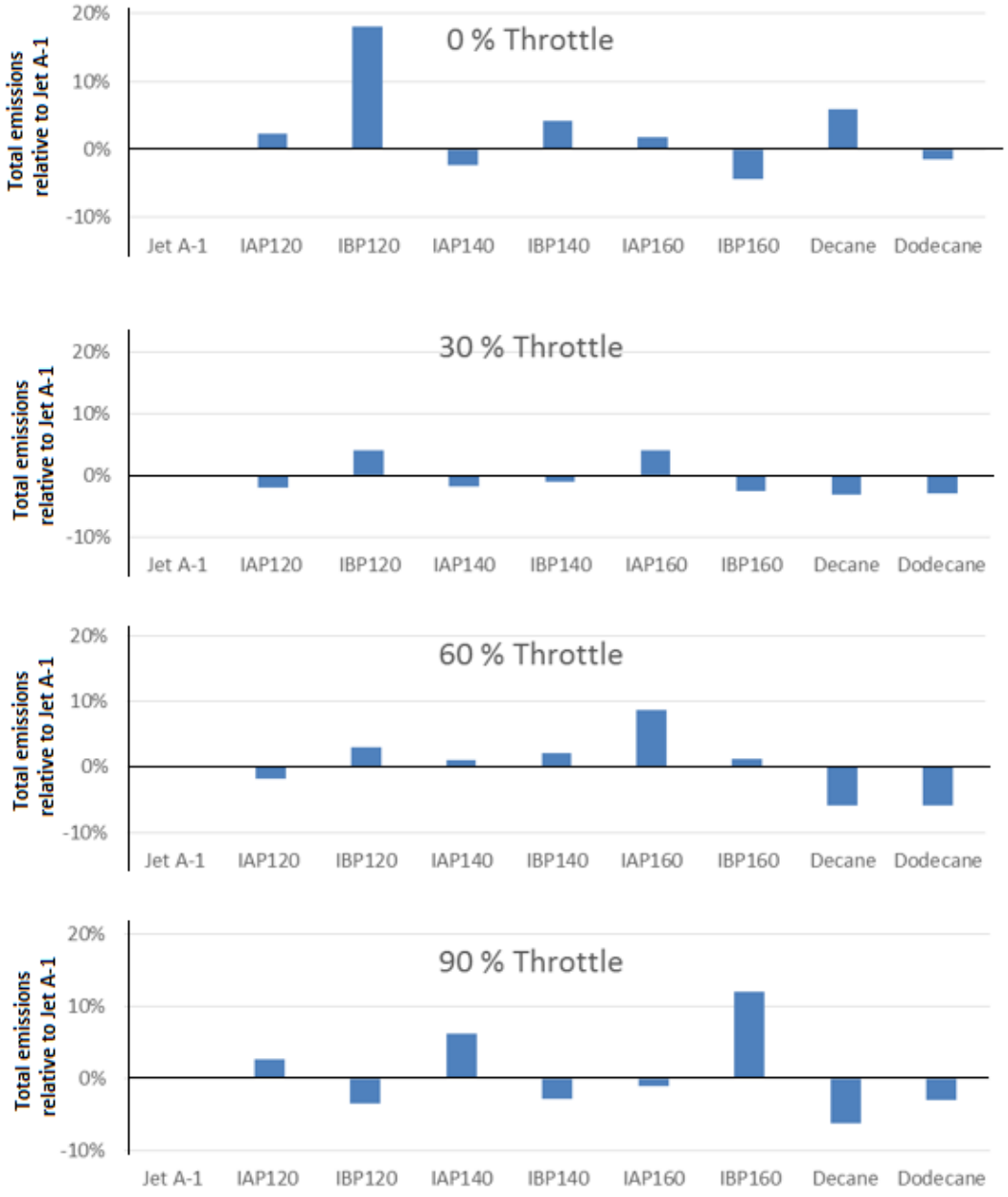

Figure 5.4-11: comparison of total emissions of all gaseous species (excluding O_2 and N_2) per unit thrust, with unblended Jet A-1 as a reference.

5.4.7 Total NO_x Emissions

An important consideration, particularly from a local air quality perspective is the amount of NO_x that is produced when using alternative aviation fuels.[24-26] NO_x formation through the combustion of fuel in an engine occurs through three mechanisms; Thermal, Prompt and Fuel sourced.[27]

Thermal NO_x is formed through the reaction of atmospheric oxygen and nitrogen at elevated temperatures, only becoming significant at temperatures over 1500 °C.[28] At high fuel:air ratios, thermal NO_x can start to contribute to total NO_x for aviation gas turbines, however for the most part, NO_x formation occurs through the 'prompt' NO_x mechanism. This occurs through the reaction of fuel derived radicals with the atmospheric nitrogen, eventually leading to nitrogen oxides.[29]

Due to the purity of reactants used in the production of the alternative fuels, there is no opportunity for the incorporation of nitrogen containing compounds and thus very little, if any of the NO_x observed will be due to fuel bound nitrogen. It is likely, however that in a fuel containing higher levels of nitrogen species elevated NOx levels would be observed.

In this investigation, between 2-6 ppm NO_x was observed for all the fuels tested (5.4-13). At low throttle settings NO_x emissions were similar for all the fuels, with 5 or 6 ppm recorded. With increased throttle and therefore a decreased fuel:air ratio this was reduced to 2-3 ppm due to a higher dilution of emissions.

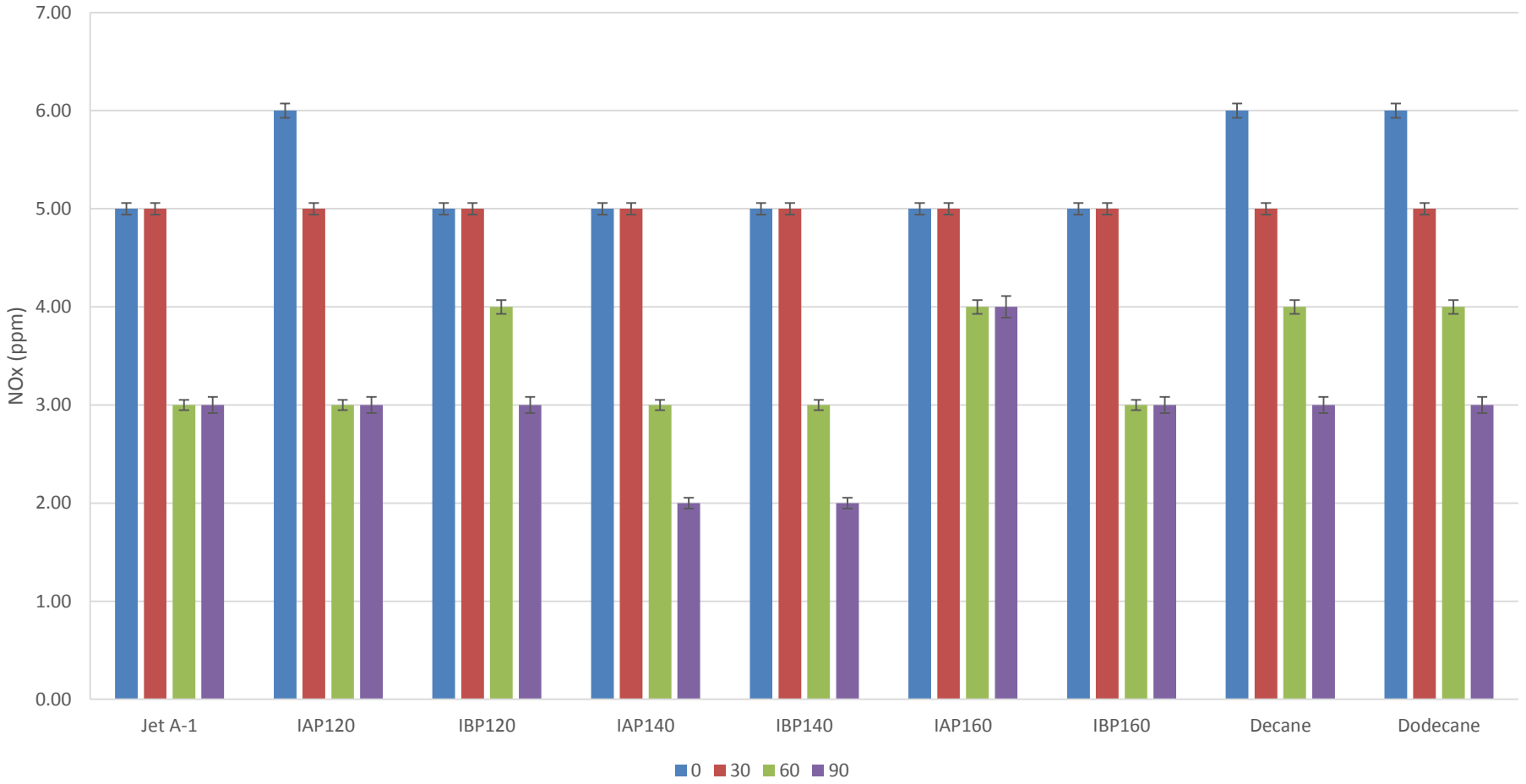

Figure 5.4-12: Total Nitrogen Oxide emissions for fuel blends at 0, 30, 60 and 90 % throttle, error bars are given as one std.deviation (n=3) of Jet A1

5.4.8 Total Hydrocarbon (THC) Emissions

Total hydrocarbon emissions in the exhaust were also measured for all the fuels examined (Figure 5.4-13)

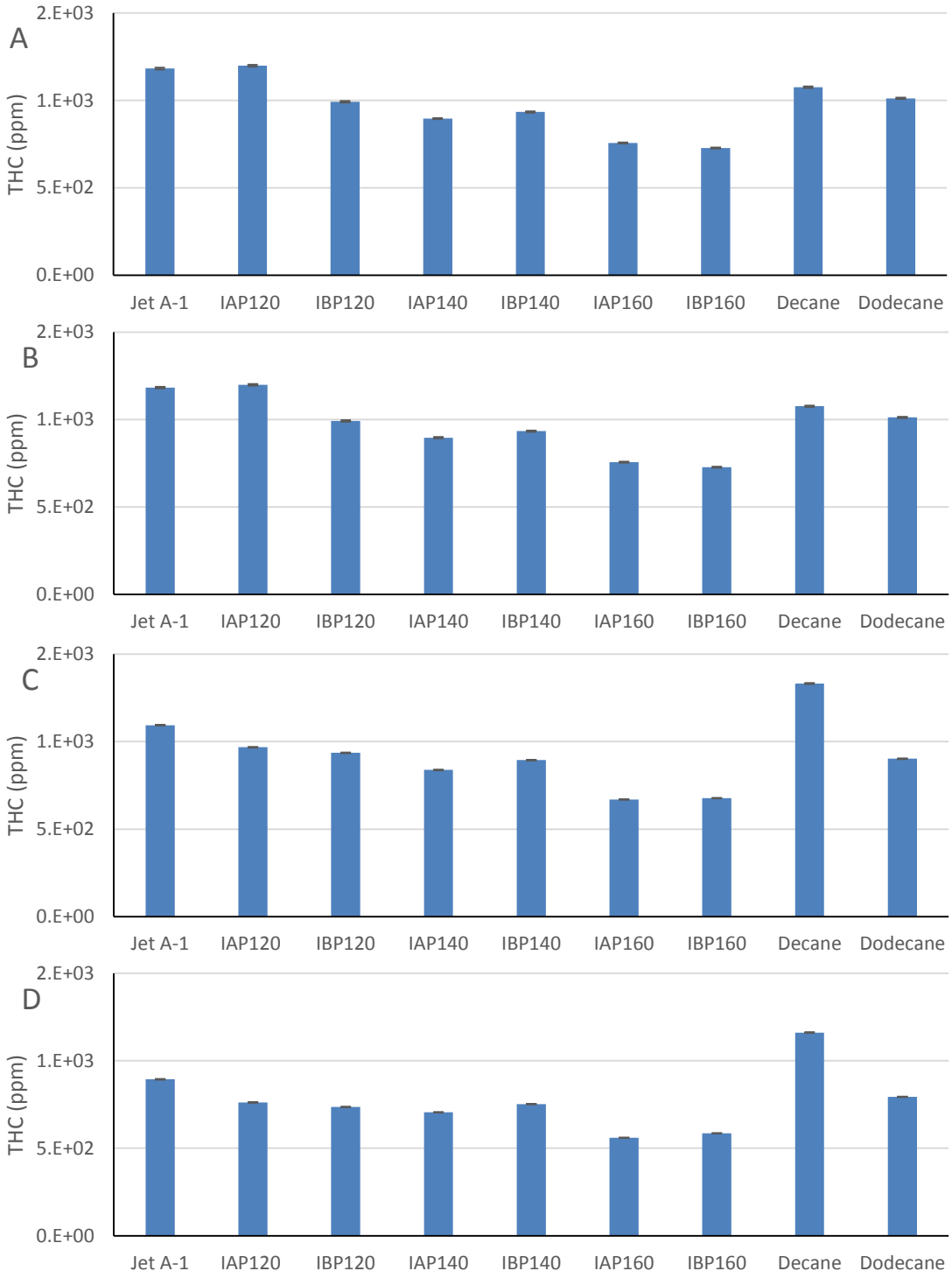

Figure 5.4-13: Total hydrocarbon emissions at 0, 30, 60 and 90% throttle (A, B, C and D, respectively). Error taken from repeatability tests using Jet A-1 and applied as standard error.

Hydrocarbon emissions from jet aircraft act as ozone precursors through formation of OH radicals and subsequent reactions with NO_x and O_2.[30-32] They also combine to form polycylic aromatic hydrocarbons which are toxic and carcinogenic when inhaled by humans and wildlife.[33-35] The minimisation of hydrocarbon content in the exhaust plumes of jet aircraft is therefore highly desirable.

The presence of large quantities of hydrocarbon species in the exhaust of a gas turbine engine is also indicative of an inefficient combustion process, this is not only undesirable from a health and safety point of view, but also indirectly, a logistical and economic one.

Considerable differences were observed between fuels at idle, with the iso-alcohol derived blends exhibiting both the lowest and highest hydrocarbon emissions. IBP160 produced a value of 618 ppm and IAP120 produced nearly twice that value at 1174 ppm. This compares with decane and dodecane which produced values of 846 and 1025ppm respectively. Unblended Jet A-1 emitted 1064 ppm total hydrocarbons at this throttle setting.

At 30% throttle the same trend is seen for the oxygenated blends, however hydrocarbon emissions from decane increases proportionally more than other fuels tested. This increased THC measurement would suggest lower quality, less complete combustion. One possibility is that, at this engine condition, the presence of the oxygen moiety within the oxygenate fuels aids combustion in a manner consistent with the findings in internal combustion engines run on oxygenated fuels. From O_2 measurements, the total emissions also appear to be lower, suggesting a more efficient utilisation of the fuel for a given thrust. Efficient combustion as is suggested by compilation of measurements at this thrust level could, to an extent mitigate the negative effective effect of a reduced gravimetric energy density of these oxygenated fuels. Conversely, these results would also seem to suggest that the combination of a 10-12 carbon alkane surrogate actually decreases combustion efficiency, with greater emissions being observed for a given throttle setting in particular, greater hydrocarbon emissions resulting from the incomplete combustion.

At 60 % throttle a marked change in hydrocarbon emissions is observed, with purely hydrocarbon fuels such as Jet A-1 and the decane and dodecane blends showing even greater elevated THC emissions relative to the oxygenate blends. This trend continues and is more evident at the highest throttle setting of 90 %.

5.5 CONCLUSIONS

The first aim of this chapter was to assess a small scale micro jet engine as a method of determining fuel characteristics on the small scale. While the testing was largely successful, and some indicative data was obtained, no conclusive trends could be observed for any of the fuels tested. The use of a micro gas turbine designed for use in an aeronautic application is suggested as a much better method to gain representative data than previous studies, which have used local power generation units. Whilst the potential of this methodology is believed to be great, there is not as yet a standardised method used for setup and emissions analysis, meaning that comparability between data sets from separate investigations is not possible. It is hoped that this investigation will add to a small, but growing experience base using these engines for the testing of alternative fuels. It is recognised that with respect to some of the less concentrated emissions, the sensitivity of road vehicle emissions testing equipment is not ideal due to high dilutions of the jet exhaust. Whilst continued testing was not possible within the available timeframe for this investigation, it is suggested that either sampling be carried out so that samples may be analysed ex-situ with more sensitive techniques, or alternatively, that more sensitive emissions analysis equipment is used in-situ.

The most notable finding, and one which was common with a similar finding of an investigation by Lupandin et al. is that whilst the oxygenate biofuels have significantly lower gravimetric energy density, at high throttle settings thrust was greater, and in the case of the aforementioned investigation, a higher BSFC was exhibited by a biodiesel blend relative to unblended diesel oil. This has significant impact for the consideration of biofuels for aviation, suggesting that perhaps the current assessment framework is too simplistic, and that the operating cycle of an aircraft engine needs to be considered when determining the requisite properties. Long durations at high thrust are potentially more suited to using oxygenated fuels.

Whilst the performance of oxygenate fuels was found to be comparable to that of jet A-1, there was no significant reduction in CO, NO_x, or CO_2. NO_x was not increased, as is generally observed in IC engine testing of oxygenates. This is attributed to the very lean operating conditions of gas turbines compared with IC engines. A small reduction in THC emissions was observed, due to the fact that the engine is optimised for the use of hydrocarbon fuels and fuels of similar volatilities.

The use of decane and dodecane blends in general, increased emissions and increased thrust at lower throttle settings. This is attributed to a more volatile boiling temperature profile and better vaporisation at lower engine temperatures. From the point of view of emissions and performance, there was no significant beneficial or deleterious effect through using these blends when compared with unblended Jet A-1. This allows for the possibility of using these fuels as blending agents, subject to further more extensive compatibility tests. The sustainability of these potential alternatives would need confirmation through a comparative life cycle assessment. It is not currently possible that these fuels would be produced solely using the biocatalytic valorisation step presented in this thesis, however this may be viable with further development.

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Chapter 6

CONCLUSIONS AND FUTURE WORK

6.1 CONCLUSIONS

The overarching aim of this thesis was to assess three different technologies for the production of an aviation turbine fuel alternative. Whilst there has been much research focussed on production of suitable alternatives for gasoline and diesel for road transport applications, this work aimed to contribute to the growing body of research focussed primarily on production of suitable aviation alternatives.

The first technology presented in this thesis was the biocatalytic carbologation of furfural and HMF, two platform chemicals derived from cellulosic hydrosylates. The combination of these 5 & 6 carbon chain length furanic molecules, allows for production of a fuel precursor of between 10 and 12 carbons, thought to potentially be suitable for blending with aviation turbine fuel. The technique investigated involved the carboligation of the two molecules in aqueous media, using 20 % DMSO co-solvent. The reaction was able to be conducted in ambient conditions, at room temperature. Whilst organocatalytic methods for the carboligation have been demonstrated previously, this is thought to be the first time that enzymatic catalysis has been utilised for the linking of HMF. As a result of these mild conditions, it would be highly likely that this technology, if developed and optimised further, would be considered a sustainable catalytic route to the valorisation of biomass derived furanics.

Whilst the primary focus with respect to this investigation was production of these molecules as potential aviation fuel precursors, their versatility was further demonstrated by co-workers. Through combination with choline chloride in a 1:1 ratio, the alpha hydroxyketone form of the ligated C12 product, was able to be used in the formation of a novel DES, with the two solids forming a viscous liquid upon combination.

This biocatalytic method, whilst in its infancy, will certainly add to a suite of conversion technologies ready to be utilised in the coming years, as the refining of biomass becomes increasingly industrially important and economically viable for a growing range of applications.

The second technology discussed in chapter 3 of this thesis is a palladium catalysed thermochemical upgrading of fermentation products. The upgrading of ABE fermentation products has previously been reported by Anbarrassan et al. in 2012, with products being suggested as potential alternative diesel fuel precursors,

requiring hydrogenation before use.[1] Whilst work on ABE fermentation has previously focussed on maximisation of single components of the product mixture, this offers a method whereby all components may be utilised, in particular the acetone component, thus maximising overall efficiency.[2]

In this investigation, the technique reported by Anbarrassan & co-workers, was used for the alkylation of a product mixture suggested to potentially be available through the metabolic engineering of the Clostridia genus of bacteria. These alternative mixtures replace n-butanol in the ABE fermentation product mixture, with isobutanol or isoamyl alcohol, both branched alcohols.[3,4] The alkylation was found to proceed well under solvent free conditions, with conversions between 54-73 and 53-86 % for isobutanol and isoamyl alcohol containing substrate mixtures, respectively. Reaction temperatures between 120 and 160 °C, with higher efficiencies observed at higher temperature.

Alkylation of branched ABE alternative mixtures allowed for the production of a complex mixture of ketones with carbon chain lengths of up to 13, with the largest product proportion being that of the double alkylates having 11, and 13 carbon ketones for mixtures including isobutanol and isoamyl alcohol, respectively. These branched ketone fuels were found to exhibit improved low temperature properties relative straight chain analogues however exhibited a lower energy density and poorer low temperature properties than those of conventional aviation fuel. Whilst catalyst reusability was found to be very poor with activity being lost after just one reuse, it is possible that with process optimisation or better catalyst regeneration this could be improved.

Engine testing of these fuel mixtures at a 50 % blend level within an AMT mercury micro gas turbine found that emissions were not significantly different to those of unblended Jet A-1. Whilst the use of oxygenates in testing on internal combustion engines commonly exhibit lower CO values and increased NO_x, this was not observed in the case of these ketone mixtures when used in a gas turbine fuel.

Overall, this technology is a valuable conversion method for ABE fermentation products and its alternatives. Crucially for the aviation industry, the work presented within this thesis, demonstrates the ability of this system to incorporate branching into potential alternative aviation fuels. Also demonstrated and of high significance to the potential sustainability of this technology, is the ability to obtain good conversions under solvent free conditions. The requirement for use of organic solvents in industrial

processes impacts hugely on the environmental sustainability, as well as economics of the process.[5]

The third technology investigated in this thesis, was a LPP system. The production of liquid pyrolysis oils has attracted much attention from the research community, however their production through liquid phase pyrolysis, less so. The system investigated is a zeolite catalysed conversion of pistachio hull biomass using a high boiling petroleum oil as a heat carrier (bp. >260 °C). The zeolite was found to catalyse the cracking of the carrier oil alongside that of the biogenic feedstock, with only up to 7 % biomass derived carbon detected in the product using ^{14}C analysis. Catalyst reuse revealed that selectivity was not changed on the second use, with 7 % modern carbon measured, however total yield was much reduced.

Physical properties of the distillate products were measured. Gravimetric energy densities were found to be excellent, with all products from all catalysts exhibiting HHV values of more than 45 MJ/kg. This is however, thought to be largely owing to the fact that only 7% of the product was derived from the pistachio hull feedstock.

Overall, this investigation demonstrated that pistachio hull waste from the food industry, may be converted to a liquid product using a liquid phase pyrolysis method utilising zeolite catalysts. Whilst conversion was evident, there remains an issue with selectivity for the bio-derived chemical species within the carrier. Until this selectivity issue is eliminated or reduced, it is highly unlikely that the resultant fuel may be regarded as sustainable, and it is unlikely that the process could be economically viable without further optimisation and minimisation of carrier oil loss.

The structure of this project was such that any alternatives produced in the laboratory, if deemed to be a potential alternative fuel candidate, were taken on to engine testing. This approach, alongside rigorous physical properties testing, allows for assertions as to the validity of the experimental hypotheses to be assesses as widely as possible, giving real performance data exposing any assumptions which may not be valid for the desired application. In this investigation, one such assumption was highlighted; that a lower HHV fuel would necessarily provide less thrust than a fuel with a higher HHV. This was found to be true at some throttle settings, however the assumption did not hold true at high throttle settings, perhaps enhancing the case for consideration of oxygenate fuels in aviation.

It is the opinion of the author, that where possible, synthetic fuels development should be coupled with performance and emissions testing at the earliest possible

opportunity to allow consideration of fuels which may have been disregarded owing to incorrect assumptions based on existing understanding of fuels engineering which is largely derived from experience with similar but not identical petroleum fuels.

6.2 FUTURE WORK

In chapter 2, the biocatalytic valorisation of furanic compounds was achieved through the utilisation of BAL. This was carried out in an aqueous medium using a DMSO co-solvent in order to solubilise the BAL. Whilst the ability of BAL to carboligate these furanic compounds was demonstrated, it is unlikely that use of DMSO as a co-solvent at industrial scales would be acceptable from an environmental sustainability point of view. It is therefore suggested that new solvent systems, incorporating less environmentally damaging solvents, such as THF and MTHF are further investigated for suitability.

The use of isolated enzymes requires the extraction from bacteria which is laborious and expensive. It is suggested that the use of whole cell catalysis should be investigated potentially with immobilisation of the cells to allow for easier and more efficient processing. This has been demonstrated for other biocatalysis methods presented in the literature, and it is possible that the same benefits may apply to this process also.6

In chapter 3, a Pd catalysed alkylation of theoretical permutations of ABE fermentation mixtures was investigated. It is suggested that the flow catalysis for this process be investigated. Whilst it is probable that the batch process could be further optimised, it is thought likely that any larger scale production of fuel through this catalytic method would be required to be in the flow configuration and similar catalytic processes have been demonstrated in flow in the literature.[7] Combination of the knowledge gained through the work presented here regarding the selectivity of these catalysts for isobutanol and isoamyl alcohol, will allow for an efficient and novel production of long chain ketones. It is suggested also that alternative catalysts should be investigated. For example, the use of rhodium, ruthenium catalysts have been shown to be active for this alkylation reaction in an aqueous medium.[8] It should be investigated whether this activity is retained in a solvent free reaction such as those presented in this work. Other transition metal catalysts such as Cu(II) and Au have been shown to be active when supported on hydrotalcite catalysts.[9,10]

The use of ketones as fuels without hydrogenation has not been considered as a general rule, with ‘oxygenate fuels’ becoming almost synonymous with ‘alcohol fuels’. It was demonstrated here that the physical properties of ketones are actually much more suited to use as an aviation (and potentially road transport) fuel than many alcohols. It is suggested then, that further investigations into the fuel properties of

ketones are investigated, with oxidative stability and hygroscopicity, in particular, being measured and reported.

In chapter 4 of this thesis, a LPP system was investigated. This technology has before now attracted very little research focus evident from review of the literature. The system was found to be able to convert pistachio hull waste to a low nitrogen liquid which may be suitable as a fuel. However, upgraded biogenic species constituted only 7% of the overall product mixture, with the majority being made up by petroleum carrier oil, cracked by the zeolite catalysts.

The system should be investigated for efficacy using lower grade carrier oils, which may be 'co-refined' simultaneously along with valorisation of the pistachio hull feedstock. Another point of investigation should be the investigation of the effect of using high grade but higher molecular weight carrier oils. From the investigation and anecdotal evidence from a pilot scale operation, there is suggestion that higher biomass loadings may lead to higher biogenic carbon content in the product distillate. This should be investigated, with a maximum loading value being determined. Typically, other investigations into LPP systems have utilised higher temperatures for biomass conversion. It is suggested that higher temperatures may allow for better dissolution of the biomass, and potentially higher biogenic carbon content within the resultant product.[11]

Engine testing of the ketone fuels and hydrogenated C10-12 fuel precursors synthesised in earlier chapters was carried out in chapter 5 using a micro gas turbine. The emissions testing equipment used was suitable for identification of any large deviations away from the values set using conventional Jet A-1, however for NO_x and CO emissions, the resolution of measurements was low, due to the exceptionally high dilution of emissions from a gas turbine relative to internal combustion engines, for which the sampling system is designed. It is suggested that further work be carried out using more sensitive equipment, with higher sampling volumes, or alternatively, that exhaust gas samples are sampled, stored and analysed ex-situ using more sensitive GC-MS equipment.

The thrust values obtained for each of the fuels were very accurate and reproducible, and gratifyingly appeared to highlight a trend of higher thrust efficiencies for oxygenated fuels at lower throttle settings. This, to the authors knowledge has not been reported before in the context of aviation gas turbines, with all research seemingly working on the basis of HHV values alone. This finding certainly warrants further investigation, with accurate fuel mass flow vs thrust measurements being

made. Focus should particularly be directed toward the behaviour of oxygenated fuels at high throttle settings, compared with hydrocarbon fuels.

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